STUDY OF CYCLOCOPOLYMERIZATION

by

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Dedicated to

the mother of Lawrence Chu

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract of a Dissertation Presented to the
Graduate Council of the University of Florida in Partial Fulfillment
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STUDY OF CYCLOCOPOLYMERIZATION

By

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Chairman: George B. Butler
Major Department: Chemistry

The well-known alternating 1:2 cyclocopolymer of divinyl ether
(DVE) and maleic anhydride (MAH) has been found to possess interest-
ing anti-tumor and biological activities. Recent research on the
structure of the cyclopolymer has raised a question about the ring
size of this cyclocopolymer. In this research program the structure
of this copolymer was reexamined by use of spectroscopic methods.
A linear, soluble copolymer was obtained by the copolymerization in
solvents with active hydrogens, such as chloroform and xylene. The
ir spectra showed the existence of both monomers in the copolymer
based on the strong bands at 1775, 1855, 1230 cm^{-1} (cyclic anhydride),
and 1090 cm^{-1} (cyclic ether).

By use of deuterated copolymers, the H-nmr peaks at δ 2.31, 3.47,
4.06, and 4.49 ppm with an area ratio of 2:1:1:1 were assigned for
the hydrogens of methylenes, methines on the backbone anhydride unit,
methines on the ring anhydride unit, and methines adjacent to oxygen
on the cyclic ether ring, respectively. Through the examination of

the possible isomeric structures of the bicyclic ring, the splitting of each peak group was further assigned for cis and trans di-substitutions on the anhydride unit.

The splitting pattern on the 300 MHz nmr spectrum of divinyl ether - 2,3-dideuteriomaleic anhydride copolymer confirmed the unsymmetrical six-membered ring structure. ^{13}C nmr spectra was discussed and was consistent with the conclusion from the H-nmr spectra.

A chair-form six-membered ring with trans isomer next to each side of the ring oxygen with a small portion of cis isomer was assigned for the structure of DVE-MAH copolymer.

Based on little or no change of the ^{13}C nmr spectra of the copolymers prepared at different temperatures, it was concluded that there was no significant change of structure caused by temperature effect. This led to the sole assignment of the six-membered ring structure of the copolymer as an energetically favored product.

A mechanism for the cyclization was proposed based on the HOMO-LUMO interaction of the comonomers and the radical intramolecular addition on the preoriented double bond. This mechanism led to the formation of six-membered ring structure of the copolymerization as the sole product.

The participation of the charge transfer complex in the cyclo-copolymerization was investigated with the divinyl ether-fumaronitrile system by light initiation. The evidence and the composition of the complex were obtained by the UV spectroscopic method. The structure of the copolymer was proposed on the basis of elemental analysis and ^{13}C nmr spectrum, as a mixture of 1:1 cyclocopolymer and 1:2 cyclo-copolymer structures, both with six-membered rings. The initiation

mechanism involving polar deactivation of excited molecules and the

propagating mechanism were proposed to explain the rate maximum

phenomena and the relation between copolymerization rate and total

concentration of the comonomers at 236 nm and 300 nm irradiation.

A consistent result was obtained by the proposal of the participation

of the CTC in both the initiation and propagation processes.

History of Cyclopolymerization and Cyclocopolymerization

It is well known that multifunctional monomers such as unconjugated divinyl monomers are crosslinking agents in vinyl polymerizations.[1] However, certain compounds, such as diallyl phthalate and ethylene diacrylate,[2] undergo cyclization during polymerization, with the result that 40-75% of the divinyl compound used is incapable of crosslinking. Butler and coworkers[3] found that several diallyl quarternary ammonium salts polymerized to yield soluble and hence linear polymers containing little or no residual unsaturation. Under the same conditions monoallyl ammonium salts failed to polymerize. To explain the unusual results, Butler and Angelo[4] proposed an alternating intramolecular intermolecular chain propagation mechanism to form a cyclic structure in the chain (eq. 1). This type of process is now commonly termed cyclopolymerization.

Since these initial investigations, a large number of 1-6 non-conjugated dienes of type I have been cyclopolymerized using appropriate catalysis to yield soluble, mostly saturated polymers with cyclic structures in the main chain.

In cyclocopolymerization, the comonomer contributes to formation of the cyclic structure along with the nonconjugated diene. Butler[5] reported the first example of cyclocopolymerization. By copolymerizing divinyl ether (DVE) and maleic anhydride (MAH), using a free radical initiator, a soluble polymer was obtained. A mechanism similar to the cyclopolymerization was proposed which is shown in equation 2.

This cyclocopolymer has been found to possess interesting biological activity.[5]

(Eq. 1)

$$X = \quad \diagdown_{CH_2}, \quad \diagdown Si \diagdown^{CH_3}_{CH_3}, \quad \diagdown Ge \diagdown^{CH_3}_{CH_3}, \quad \diagdown NR, \quad \diagdown N \diagdown^{R_1}_{R_2},$$

$$\diagdown P \diagdown^{O}_{R}, \quad \diagdown O, \quad \diagdown S, \quad \diagdown SO_2$$

+ R· $\xrightarrow{\text{Initiation}}$

Intermolecular
propagation

$\xrightarrow{\text{Intramolecular Cyclization}}$ (Eq. 2)

Intermolecular propagation

$\rightarrow$ $\Rightarrow$ $\Rightarrow$
Alternate repetition
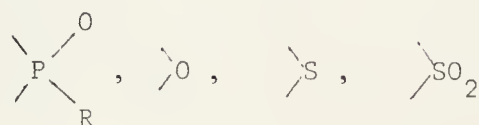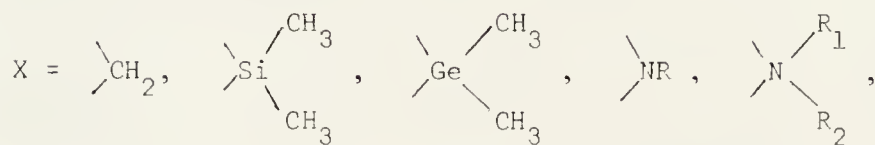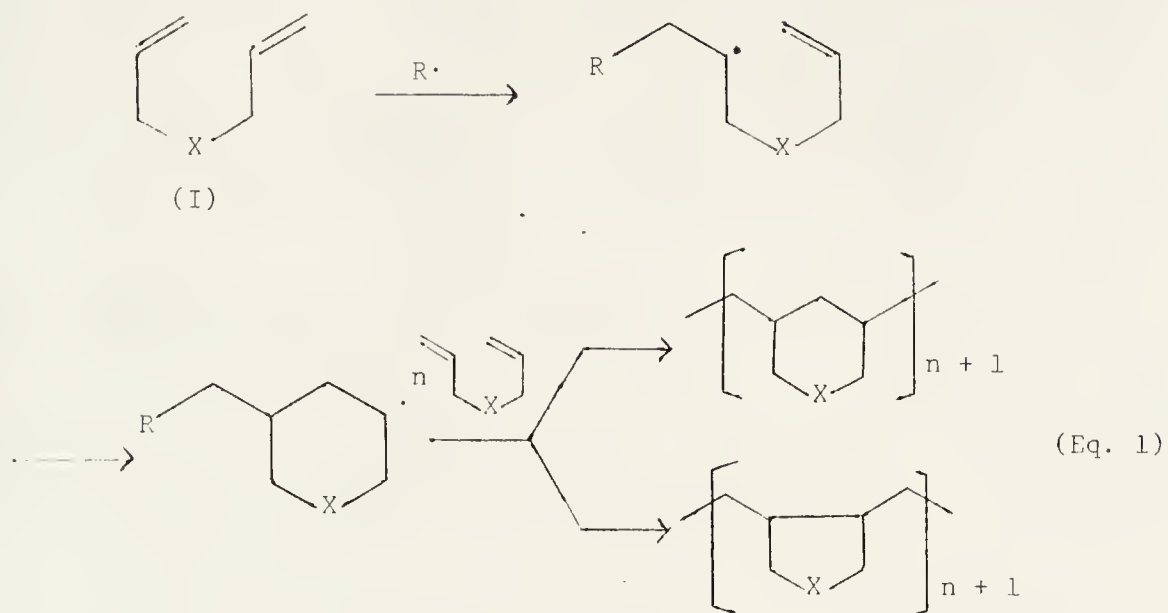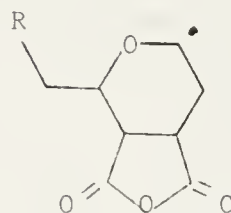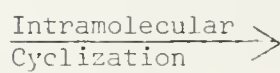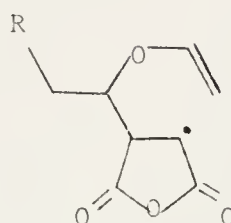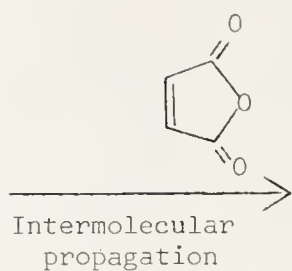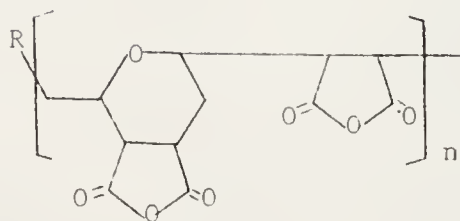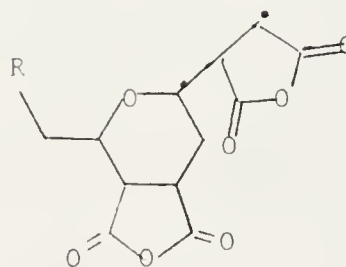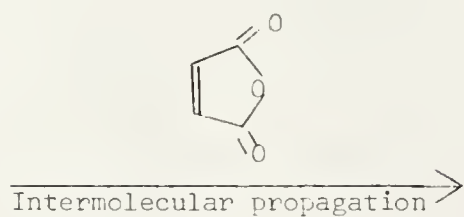
The proposed mechanism was based on the following facts:[6] (a) a soluble copolymer was formed, (b) little or no residual unsaturation was detected in the copolymer and characteristic absorption bands for cyclic anhydride and ether were observed in infrared spectra, (c) the composition of the copolymer was close to a diene-olefin molar ratio of 1:2 over a wide range of comonomer feed composition, (d) quantitative conversion to copolymer was obtained, (e) the cleavage by hydriodic acid and the incorporation of iodine into the copolymer indicated the presence of cyclic ether groups, and (f) neither monomer homopolymerizes readily under the same condition as copolymerization.

Following Butler's discovery, the copolymerization reactions for a wide variety of 1,4-dienes and olefins have been reported. Butler and coworkers further studied some mono-olefin-1,4-diene systems to produce 1:2 (1,4-diene:monoolefin) copolymer with generalized structure II.

$$X = \ \backslash O, \quad \backslash SO_2, \quad \backslash Si \ / \ CH_3 \ CH_3$$

$$Y = -CN \ or \ Y-Y =$$

(II)
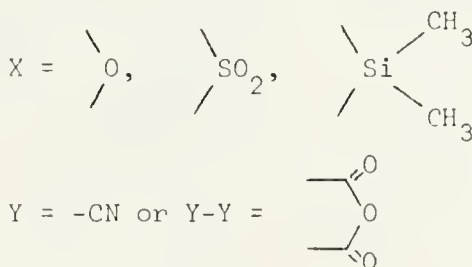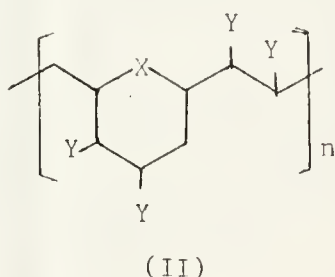
Stille and Thomson[7] prepared, with a variety of free radical initiators, a soluble copolymer of a nonconjugated diene, 1,5-hexadiene, and sulfur dioxide. Elemental analysis of the copolymer samples substantiated the existence of a material containing exactly two sulfur dioxide portions to one of diolefin. The six-membered ring structure was confirmed by comparing the ir spectra of the copolymer sample with pentamethylene sulfone.

$$\left[\begin{array}{c} \text{(structure III)} \end{array} \right]$$
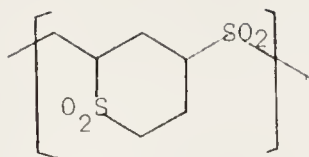
III

Price and coworker[8] prepared the copolymers of N,N-divinyl aniline with diethyl fumarate in bulk and solution with azobis-isobutyro-nitrile (AIBN) at 60°C. Diethyl fumarate, having widely different polarity from that of divinyl aniline, and being reluctant to homo-polymerize, polymerized with divinyl aniline in widely different monomer concentration ratios to give copolymers of nearly constant 2:1 molar ratio composition. The colubility of this copolymer and the negative results of analysis for residual double bond by infrared absorption in the 6.0-6.2 µ region, supported the cyclic copolymer structure IV.

$$\left[\begin{array}{c} \text{(structure IV)} \end{array} \right]$$
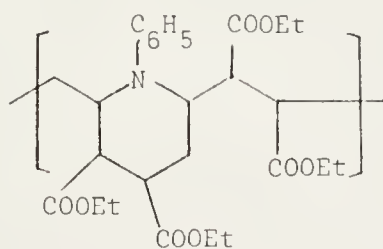
IV

The copolymerization of divinylphenylphosphine with acrylonitrile was studied by Butler, et al.[9] The copolymer produced was soluble in DMF and showed no residual unsaturation. Elemental analysis indicated the copolymer contained 0.265 mole fraction of divinylphenylphosphine and 0.732 mole fraction of acrylonitrile. The structure of this copolymer and the reaction for its formation are as follows (eq. 3):
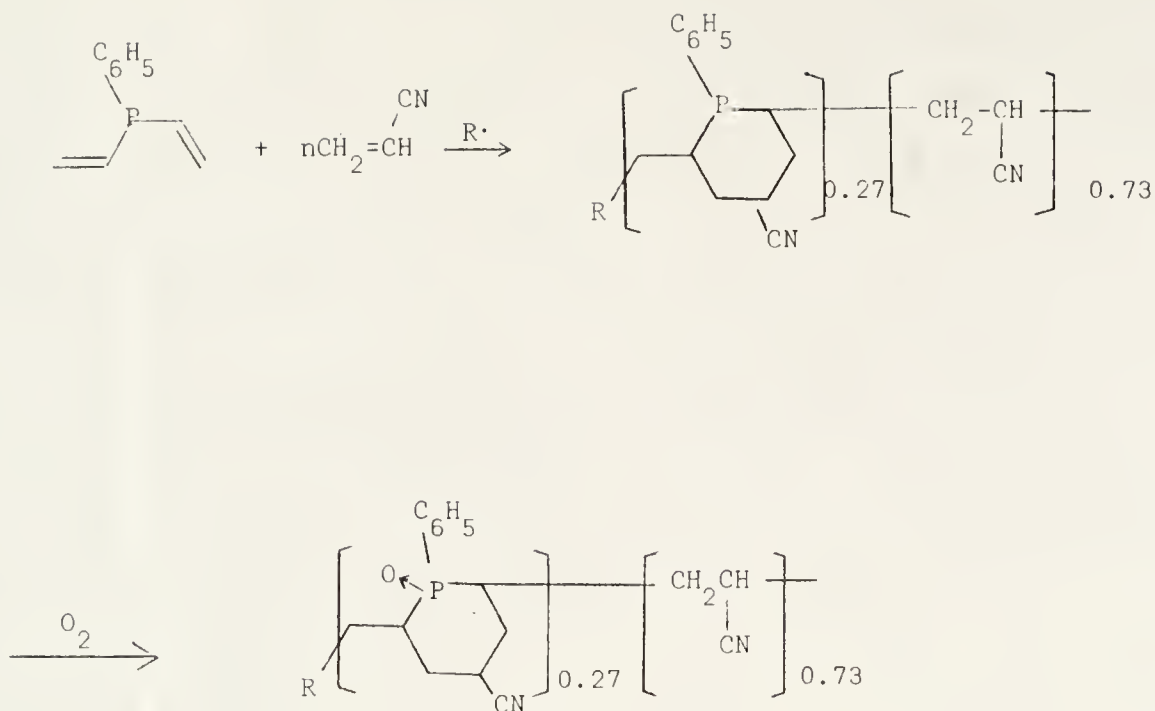
Rigid or multicyclic systems have been reported. Meyersen and Wang[10] prepared several copolymers of fused ring systems such as bicyclopentene with sulfur dioxide or maleic anhydride in solution by free radical initiation. Copolymer was obtained in the ratio of 1:2 as in structure V in equation 4.

X = SO₂   or

Eq. 4
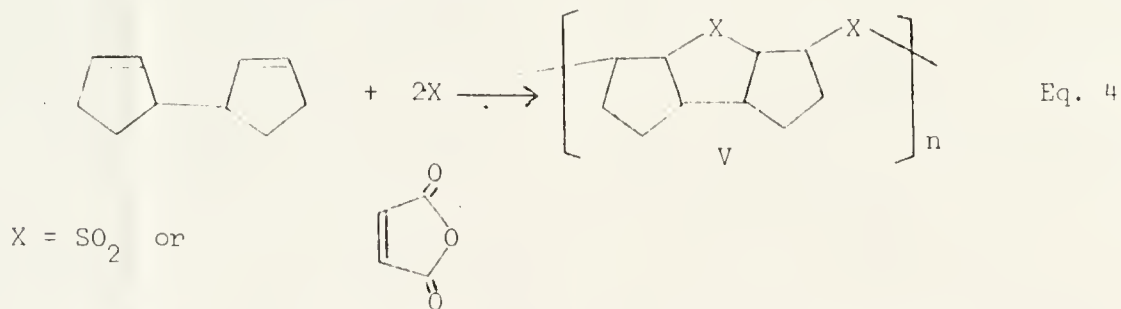
Yamaguchi and Ono[11] reported the copolymerization of sulfur dioxide and dicyclopentadiene (DCPD) in liquid sulfur dioxide with AIBN or other radical initiators at o° or 20°C. Soluble copolymer was obtained with a composition ratio of DCPD to sulfur dioxide of 1:2, and containing

virtually no residual double bond. The structure of this polysulphone
was proposed as VI.

VI
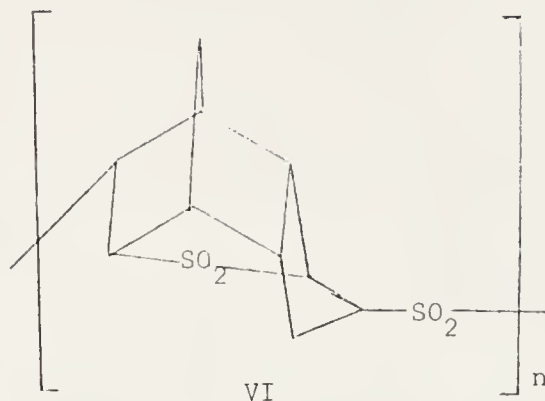
Butler and Pledger[12] proposed 1:1 alternating copolymer of maleic anhydride
with 5-ethylidene-, 5-methylene-, and 5-vinyl-bicyclo(2,2,1)-2-heptene.
Evidence supported a tricyclic structure which incorporated maleic
anhydride as part of a six-membered ring repeating unit, for example
structure VII.

VII
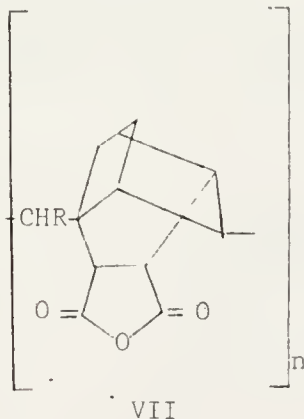
The essential structure of the cyclocopolymers were proposed based
on the following methods.

1. Elementary analysis - Most of the copolymers which have been studied
have a 1:1 or 1:2 comonomer composition in the copolymer regardless of
the wide range of feed composition, solvent, or initiator concentration.

2. Little or no residual absorption in carbon carbon double bond -
This indicates that all the double bonds in the diene were incorporated

into the copolymer. Only high degree of cyclization and crosslinking

can explain this observation. The residual unsaturation can be

detected by the absence of, or little ir absorption in the 6.0 to 6.2 μ

region and nmr. Negative results of catalytic hydrogenation has been

used to show the absence of residual carbon carbon double bond in the

copolymer.

3. The solubility of copolymer and the absence of gelation at high

conversion rule out the crosslinked structure.

4. Existence of both monomers in the resulting polymer - This can be

shown by the characteristic absorption bands of the comonomers in the

infrared spectra. For example, the 1100-1085 cm^{-1}, strong, broad band

for cyclic ether and the 1860, 1795 cm^{-1} bands for cyclic anhydride in

the ir spectra of DVE-MAH copolymers indicating the existence of both

comonomers in the copolymer.

5. The alternating ratios are always supported by elementary analysis.

Chemical method may support the proposed structure. Butler and

Guilbault[13] hydrolyzed and dehydrohalogenated the copolymer of DVE-

chloromaleic anhydride, followed by the treatment with $KMnO_4$ to get the

vic-diol copolymer. The degradation result of this vic-diol copolymer

upon periodic acid cleavage supported the 1:1 structure with only DVE

units on the backbone.
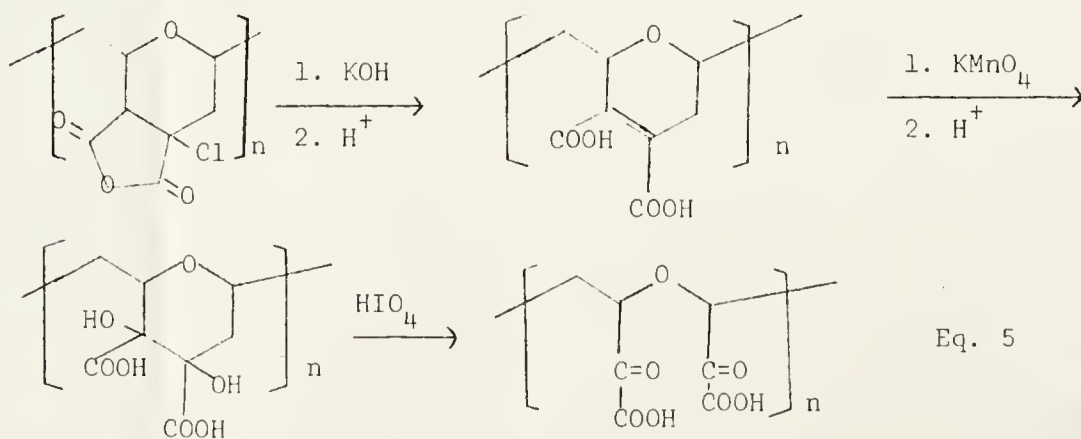
Eq. 5

Both five- and six-membered rings can be formed during the cycliza-
tion step. Unfortunately not much work has been done along this line
to distinguish between these possibilities.

Stille and Thomson[7] used the ir absorption spectra of model compounds,
VIII and IX, to compare with the 1,5-hexadiene-sulfur dioxide copolymer.
They concluded that the six-membered ring structure (III) was present in
the copolymer.
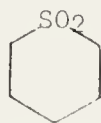
VIII   IX

This method has also been used by Meyersen and Wang[10]   in their
fused ring system-sulfur dioxide copolymer as mentioned in the last
section.

Butler and Fujimori[14] studied ring size by the readiness of the dehy-
drohalogenation of the cyclocopolymer. The quantitative elimination
of only half the chlorine content of dichloro-maleic anhydride-DVE
cyclocopolymer provided the first support for the proposed six-membered
cyclic repeating unit. There would have been no such elimination if the
repeating unit were five-membered. If both the halogens and the
hydrogens at the 2-position to the oxygen were eliminated, the product
would be a furan derivative which should be detectable due to its
aromatic character.

Eq. 6

Eq. 7
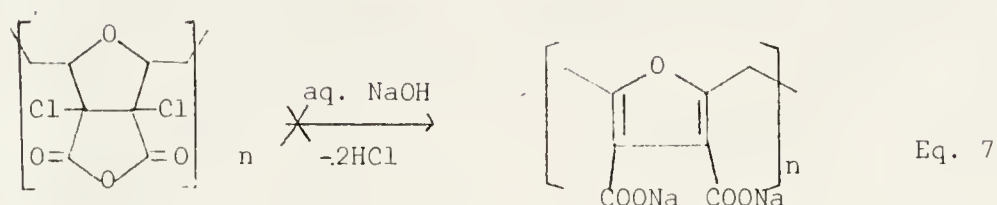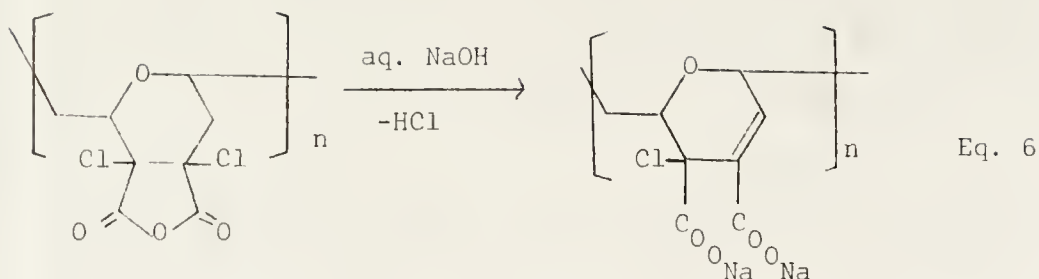
On the other hand, the ring structure of the cyclopolymer has been intensively investigated by chemical and spectroscopic methods. Butler, Crawshaw and Miller[15] conclusively proved the existence of cyclic structure of cyclopolymer prepared by free radical initiation for diallyl quaternary ammonium salts. A nondegraded polymer was obtained by treatment with $KMnO_4$. However, the ring size was not determined by these authors. Later, by ^{13}C nmr spectroscopy,[16] both the five- and six-membered rings were found in these cyclopolymers by comparing with model compounds. Dehydrogenation of the cyclopolymer followed by the identification of the resulting aromatic rings enabled Marvel and Vest[17] to confirm the six-membered ring structure in the cyclopolymer of 2,6-dicarbomethoxy-1,6-heptadiene prepared by free radical initiation.

Eq. 8
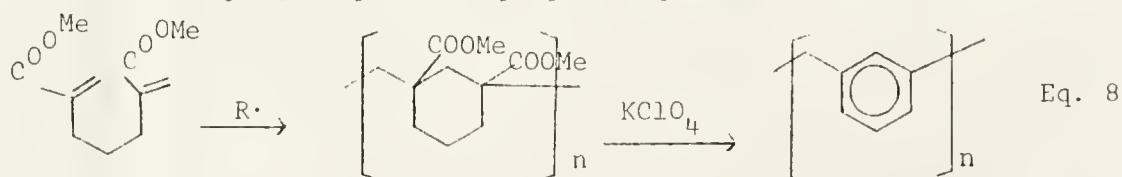
Spectroscopic methods have been applied to studying the ring size for the cyclopolymer. Butler and Myers[18] used both ir and nmr spectroscopy to analyze the cyclopolymer obtained from dimethacrylamide and its N-methyl and N-phenyl derivatives. They found that the polymers were composed of both five- and six-membered rings. Electron spin resonance studies[19, 20] have shown that the radicals from N-substituted N,N-diallylamine in the presence of $TiCl_3/H_2O_2$ or $TiCl_3/N_2NOH$ initiation are five-membered ring cyclic species. It is possible that the radicals involved in polymer formation have very short lifetimes (thereby not detectable by ESR) and those radicals which are detectable are stable but non-propagating species.

The extended chemical shift range, the absence of the simplicity of proton decoupled ^{13}C nmr spectra, in which each carbon resonates as a singlet, makes the ^{13}C nmr spectroscopy extensively useful for study of polymer structures. Johns, Willing, Middleton, and Ong[21] used the ^{13}C natural abundance pulsed Fourier transform nmr spectroscopy to distinguish the different structure features of the polymers formed by radical induced cyclopolymerization of a series of N,N-diallyl amines by comparing with the model compounds. The polymers of N,N-diallylamines all contained cis and trans substituted pyrrolidine rings with the ratio 5:1. The polymers of N,N-bis(2-allyl)amine gave complex spectra due to the presence of both cis and trans pyrrolidine and piperidiene rings.

Mechanisms of Cyclopolymerization

Since the discovery of cyclization in the cyclopolymerization, many studies have been made on the nature of the cyclization step by theoretical consideration and experimental methods.

A statistical approach to cyclopolymerization was taken by Butler and Raymond.[22] They concluded that to explain the high degree of cyclization at high monomer concentration (Table I), a more favorable pathway from 1,6-diene to cyclic polymer might exist than would be predicted on a purely statistical basis.

Table I
The Relation Between Cyclization
and Concentration

Monomer	Conc. m/l	Cyclization %	Assumed Conc. m/l	Cyclization %
Diallyl quaternary ammonium salts	>5.0	96-100	pure monomer	<50
Diallyl silanes	1.2-2.3	>95	1.00	70
Acrylic anhydride	∿8.0	98-100	0.10	96
Diallyl phosphine	bulk	100	0.001	100

Gibbs and Barton[23] explained this by considering the presence of the large pendant group which would tend to prevent intermolecular reaction and will frequently be presented to the reactive species in a conformation which is favorable for polymerization (cyclization). Butler et al.[24] studied the effect of the stability of the cyclized radical on the rate of cyclopolymerization. The overall rates of divinyl monomers were considerably greater than that of the corresponding monovinyl monomers, the ratios varying from 2 to 10. They estimated the effective concentration of the intramolecular double bond with respect to the radical propagation, and values greater than 20 M at 50°C were obtained. This incredible effective concentration indicated that a considerable preorientation prior to reaction exists. This favorable preorientation may be related to an electronic interaction between the developing

radical site and the intramolecular double bond or in the ground state before the initiation as proposed by Butler.[25]

In an effort to explain the strong polymerization of 1,6-heptadienes relative to their monoolefinic counterparts, Butler[25] proposed that an electronic interaction between the unconjugated double bonds of 1,6-dienes or between the intramolecular double bonds and the reactive species after initiation might exist.
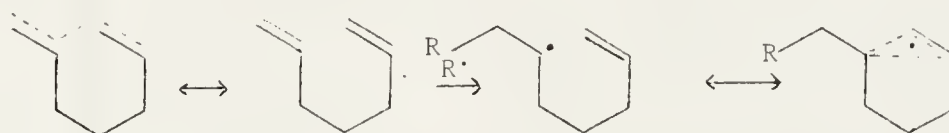
These interactions would reduce the entropy change in going from the ground state to the activiated state required for the intramolecular propagation. The ground and activated state energies both would be reduced. Mikulasova and Hvirik[26] calculated the total activation energy for radical polymerization of diallyldimethylsilane and found it to be ca. 9 Kcal/(mole double bond) less than that for allyltrimethylsilane. The electronic interaction is supported by UV absorption evidence,[27] but it is not necessary for cyclopolymerization as shown by Gibbs.[28] They found that in the case of methacrylic anhydride versus methacrylic acid, there was essentially no difference in total activation energies in the polymerizations. Marvel and Stille[29] obtained a cyclic polymer from 2,5-dimethyl-1,5-hexadiene, and suggested an unusual driving force from diene monomer to cyclic polymer.

The activation energy for cyclization is not necessarily smaller than the intermolecular addition for same radical as shown by several authors based on the kinetic scheme developed by Mercier and Smets.[30]

They derived the kinetic relationships between intramolecular and
intermolecular propagation for the free radical polymerization of
acrylic anhydride.
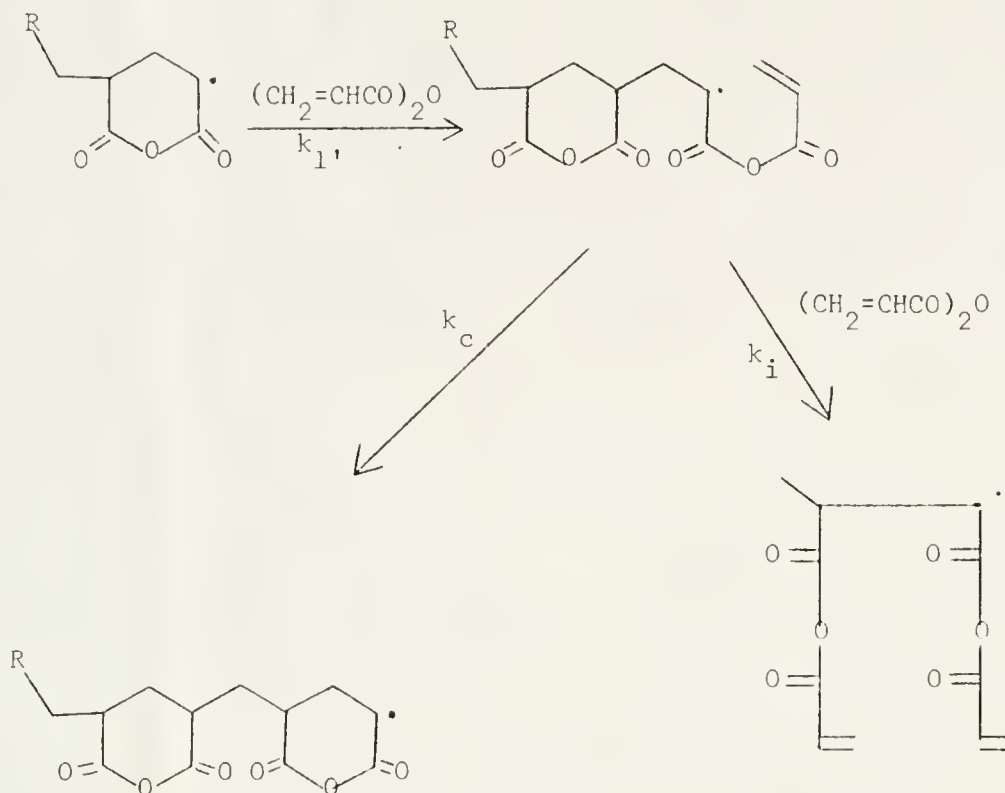
Eq. 9

The rate ratio of the intermolecular propagation (R_i) to the intra-
molecular propagation (R_c) was derived;

$$R_i/R_c = 2 \, [\text{monomer}] \, \frac{A_i e^{-E_i/RT}}{A_c e^{-E_c/RT}}$$

where the difference in activation energies ($E_c - E_i$) can be calculated.
Several $E_c - E_i$ values are listed in Table II. These results indicated
that the intramolecular propagation step requires greater energies

than the intermolecular step ($E_c > E_i$). However, the rate of cyclization is considerably larger than for intermolecular propagation ($k_c/k_i > 1$). The values for the ratio A_c/A_i indicated a high entropy factor favoring cyclization. The decrease in entropy for a cyclization step would perhaps be expected to be smaller than that for addition of a new monomer unit. Only rotational motion will be lost in cyclization; on adding a new monomer molecule to the chain, the loss of translational and rotational degrees of freedom will result. Therefore, as far as entropy is important, cyclization would be favored over intermolecular propagation.

Table II
The Energetic Parameters for Cyclopolymerization

Monomers	$E_c - E_i$ Kcal/mole	A_c/A_i mole/l	k_c/k_i mole/l
Acrylic anhydride	2.4	167	5.9
o-Divinyl benzene	1.9	50	2.8
Diallyl phthalate	0.3		
Methacrylic anhydride	2.6	256	2.4

Guaita[31] has studied the temperature independent factor of cyclization parameters for the free radical copolymerization of acrylic anhydride and divinyl ether. The results indicated that the high fractions of cyclization in cyclopolymers from symmetrical unconjugated dienes can be thermodynamically accounted for by an entropic effect largely exceeding the energetical one. The entropy decrease was smaller in the intramolecular reaction than in the intermolecular reactions.

These entropic effects are consistent with Butler's[25] postulation of the preorientation of two double bond by electronic interaction in both

ground and activated states. The nature of this preorientation between the double bonds has been though to be due to a charge transfer complexation in the copolymerization, especially in the cyclocopolymerization to produce alternating copolymers.

Mechanism of Cyclocopolymerization

Barton and Butler[32] described a general copolymerization composition equation of 1,4-dienes and monoolefins where the cyclic repeating unit is bimolecular in construction. The kinetic scheme considered is shown in equation 10.

$$
\begin{array}{ll}
m_1^\cdot + M_1 \xrightarrow{k_{11}} m_1^\cdot & \qquad m_3^\cdot + M_2 \xrightarrow{k_{32}} m_2^\cdot \\[2mm]
m_1^\cdot + M_2 \xrightarrow{k_{12}} m_3^\cdot & \qquad m_c^\cdot + M_1 \xrightarrow{k_{c1}} m_1^\cdot \\[2mm]
m_3^\cdot \xrightarrow{k_c} m_c^\cdot & \qquad m_c^\cdot + M_2 \xrightarrow{k_{c2}} m_2^\cdot \qquad \text{(Eq. 10)} \\[2mm]
m_3^\cdot + M_1 \xrightarrow{k_{33}} m_1^\cdot & \qquad m_2^\cdot + M_1 \xrightarrow{k_{21}} m_1^\cdot \\[2mm]
 & \qquad m_2^\cdot + M_2 \xrightarrow{k_{22}} m_2^\cdot
\end{array}
$$
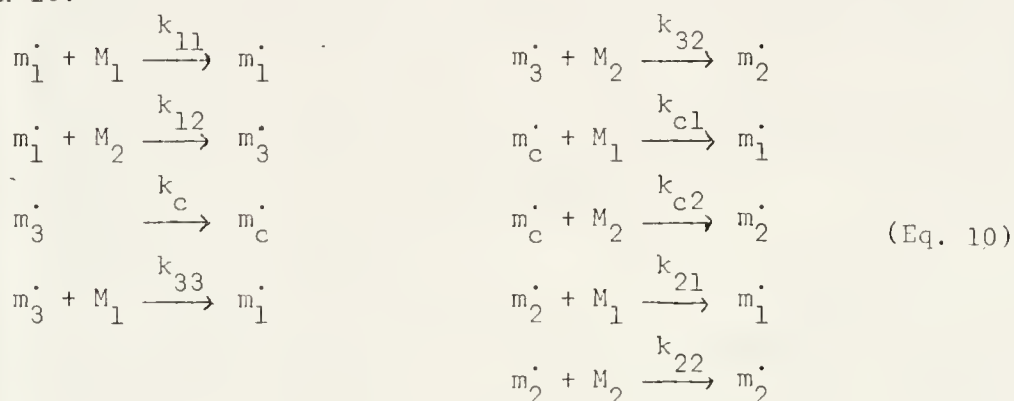
M_1 is the diene $CH_2=CH-X-CH=CH_2$ where X is CH_2, O, SO_2, etc. M_2 is the monoolefin, $CHY=CHZ$. The $m_1^\cdot$ is the radical, $-CH_2CHXCH=CH_2$, $m_2^\cdot$ is the radical $\sim\sim CHYCHZ$, $m_3^\cdot$ is the uncyclized radical
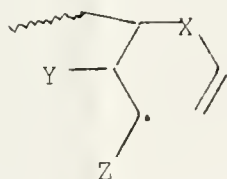
and $m_c^\cdot$ is the cyclized radical
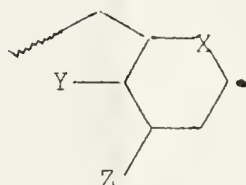
A five-membered ring structure for $m_c^\cdot$ is possible.

The derived equation which related copolymer composition to monomer feed composition in terms of five reactivity ratio parameters was given as equation 11.

$$n = \frac{(1 + r_1 x) [\frac{1}{M_2} + \frac{1}{a} (1 + \frac{x}{r_2})]}{\frac{1}{a} [\frac{x}{r_3} + \frac{r_3}{x} + 2] + \frac{1}{M_2} [1 + (1 + \frac{r_2}{x})(1 + r_c x)^{-1}]} \qquad \text{(Eq. 11)}$$

where $x = M_1/M_2$ is the mole fractional ratio of monomers in the feed, $n = m_1/m_2$ is the mole fractional ratio of monomers in the copolymer at low conversion, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, $r_3 = k_{32}/k_{31}$, $r_c = k_{c1}/k_{c2}$, and $a = k_c/k_{32}$. The equation may be approximated to simpler forms in the following cases.

a. If $k_c >> k_{32}$ so that a is very large and cyclization is the predominant reaction of the radical, m_3, the equation (11) gives

$$n = (1 + r_1 x)(1 + r_c x)/[r_c x + (r_2/x) + 2] \qquad \text{(Eq. 12)}$$

This is equivalent to considering the addition of monoolefin to diene radicals to be a concerted bimolecular step proceeding through a cyclic transition state and producing the cyclic repeating units.

b. If in addition there is a strong alternating tendency so that $r_1 \simeq r_2 \simeq r_c \simeq 0$ then equation (11) reduces in the limit to n= 1/2. This predicts an alternating copolymer composition of 2:1 molar in contrast to 1:1 for the similar limiting case of the classical binary copolymer composition equation and that for the cyclopolymer composition equation.[33, 34]

c. If the diene has a negligible tendency to add to its own radicals and $r_1 \simeq r_c \simeq 0$ and there is also predominant cyclization, then equation (12) gives

$$n = 1/[r_2/x) + 2] \qquad \text{(Eq. 13)}$$

All three cases have been found as in Table III.[32]

Table III
The Reactivity Ratio of Copolymerization

| System | Case a | | | Case b | Case c | |
	r_1	r_2	r_3	System	System	r_2
DVE-AN	0.024	0.938	0.017	1,4-PD-MAH	1,4-PD-AN	1.13
DVS-AN	0.364	0.067	0.067	DVE-MAH	DM-1,4-PD-AN	3.31
				DVE-PMI	DVE-4-VP	32.0

DVE = Divinyl ether; AN = Acrylonitrile; 1,4-PD = Dimethyl-1,4-penta-
diene; MAH = Maleic anhydride; PMI = N-Phenyl maleic imide;
4-VP = 4-Vinyl pyridine: DVS = Divinyl sulfone; DM-1,4-PD =
Dimethyl-1,4-pentadiene.

In cases (b) and (c) very low values for r_c have been reported. This low value is remarkable in the case of monomers such as acrylnitrile, and indicates that almost all the AN radicals in $m_3^{\cdot}$ react to form a ring. The actual ring formation may be either a stepwise reaction or a concerted reaction to form the product. Orientation of monomers _via_ a charge transfer complex (CTC) prior to free radical reaction explains this unusual cyclic structure and also accommodates the kinetic data (eq. 14).

(Eq. 14)
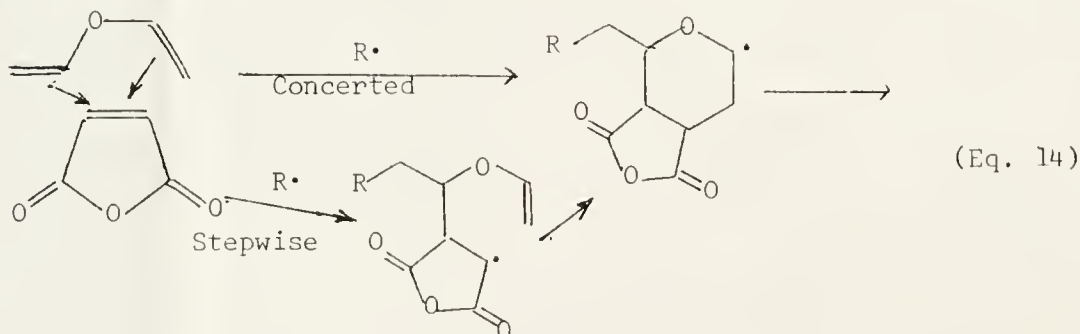
Evidence for the participation of a CTC in the copolymerization between styrene and MAH was presented by Tsuchida and Tomono.[35] They concluded that the CTC and uncomplexed MAH took part in the copolymerization. Evidence for participation of a CTC in the cyclocopolymerization of 1,4-dienes with monoolefin was presented by Butler and Joyce[36] on the comonomer pairs, DVE-MAH, DVE-MI, DVE-FN and dihydropyran (DHP)-MAH. Butler and his group have intensively studied the participation of CTC in cyclocopolymerization. The evidence of the existence of the CTC was confirmed by both UV and nmr spectroscopies. The equilibrium constant of the complexation can be obtained by these spectroscopic methods. The complex is formed by interaction of an electron-rich donor (D) and an electron-deficient acceptor (A).

$$D \ + \ A \ \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \ [D\cdot^+, \ A\cdot^-]$$
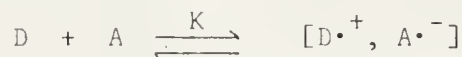
The composition of all the complexes formed by 1,4-diene and monoolefins were 1:1 complexes. The alternating copolymer compositions found were 2:1 in olefin to 1,4-diene ratio for most of the 1,4-dienes with MAH or FN. This is consistent with the postulation that the CTC undergoes a 1:1 alternating copolymerization with the electron acceptors such as MAH and FN, which can thus account for the structure of the copolymer. Some 1:1 copolymer has been obtained which can be considered as the product of the homopolymerization of the 1:1 complex.

One necessary requirement for these alternating copolymerizations is that neither of the comonomers should be homopolymerizable to a significant extent under the same condition of the copolymerization. If the acceptor is homopolymerizable such as AN, MMA and 4-VP, acceptor will

be incorporated in the copolymer to a greater extent than the expected
value for 2:1 copolymer, i.e. 67%.

The contribution of complex can be further demonstrated by
terpolymerizations. The terpolymerization of styrene, MAH, and
2-chloroethyl vinyl ether (ChEVE) studied by Tsuchida and Tomono[35]
can be explained by treating the system as a copolymerization of two
complexes, styrene-MAH and ChEVE-MAH.   Butler and Campus studied the
terpolymerization of DVE-MAH-AN system.[37] The DVE-MAH ratio in the
terpolymer was always less than 1:1 and had a lower limit of 1:2
regardless of the feed ratio of the termonomers. These results were
interpreted in terms of the participation of the CTC of DVE-MAH in the
copolymerization process with either MAH or AN.

The MAH reacted with DVE in the absence of normal radical initia-
tion to form cyclic 2:1 copolymer.[38] It was postulated that initiation
via a molecular complex occurred (eq. 15).

$$D + A \rightleftharpoons [D^{\overset{+}{\cdot}}, A^{\overset{-}{\cdot}}] \begin{cases} \overset{\cdot}{D} - A\cdot \\ D^{\overset{+}{\cdot}} + A^{\overset{-}{\cdot}} \\ {}^{+}D - A^{-} \end{cases} \quad \text{(Eq. 15)}$$

· Active forms
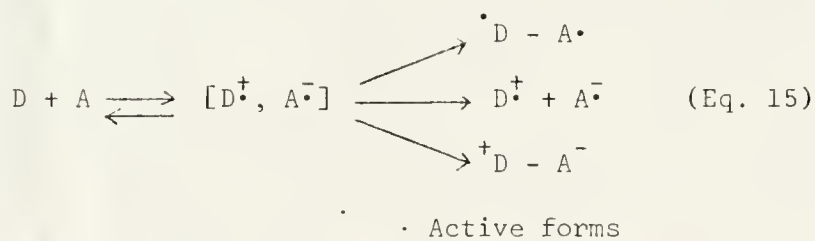
The initiation of CTC can be demonstrated by photo-initiation of this
system and the DVE-FN system. Zeegers and Butler[39] photo-initiated the
DVE-FN system with different wavelengths. They showed that both the
complex formed between DVE and FN and the noncomplexed species were
able to initiate the polymerization by light initiation.

Miller and Gilbert[40] observed that vinylidine cyanide spontaneously
copolymerized with vinyl ethers when the two comonomers were mixed at

room temperature. Yang and Gaoni[41] observed that 2,4,6-trinitrostyrene
as the acceptor monomer spontaneously copolymerized with 4-VP as the
donor monomer. Butler and Sharp[42] reported the spontaneous copolymeriza-
tion of DVE and DVS.

The concerted cyclization has been argued by Butler and
Guilbault.[13] They found that chloromaleic anhydride copolymerized
with DVE to form soluble copolymers of 1:1 composition with no residual
unsaturation. The ease with which the copolymer underwent dehydro-
halogenation indicated that the hydrogen and chlorine atoms on the
anhydride unit are in a trans configuration as a result of a stepwise
cyclization process.

The steric effect of highly substituted acceptors, tetrahydro-
naphthoquinone (THNQ) and dimethyltetrahydronaphthoquinone (DMTHNQ) on
the copolymerization with DVE was studied by Fujimori and Butler.[43]
They found that the copolymers was in constant 1:1 composition regard-
less of the feed composition. A terpolymerization of these two acceptors
with DVE was studied. Both the copolymerization and terpolymerization
and the composition can be explained by assuming that competition
between an acceptor monomer and the CTC towards the cyclized DVE radical
in the propagation step appears to favor the CTC in CTC mechanism.
These authors[14] studied the steric effect of substituted MAH on the
copolymerization with DVE. They found that (i) a strong complex gave
1:1 cyclocopolymer having a copolymer backbone consisting of only DVE
units, (ii) a sterically hindered acceptor would produce 1:1 cyclocopolymer,
and (iii) a weak CTC and reactive acceptor would produce 1:2 cyclocopolymer.
They did not mention the reactivity change of the acceptor due to the
substitution. The alternating tendency and the rate increased by using

a large amount of $ZnCl_2$ with the DVE-FN system. A 1:2 alternating
copolymer was obtained spontaneously. This system studied by Butler
and Fujimori[44] was consistent with the participation of a CTC in the
copolymerization mechanism.

Solvent effects have been studied by Butler's group.[38] The K
value (equilibrium constant of CTC formation) decreased with increase
of the dielectric constant of the solvent for MAH-DVE system. The
rate of the copolymerization and number average molecular weights
decreased in more polar solvents. In all cases, 2:1 copolymer resulted.
The study of the initial rate as a function of the feed composition[45]
made it possible to determine the relative value of the different pro-
pagation reaction rate constants consistent with a mechanism by successive
and selective addition. However, participation of the CTC in a competing
mechanism with the above cannot be completely excluded.

In conclusion, a large portion of the evidence favors the partic-
ipation of CTC in both the initiation and the propagation steps in the
alternating cyclocopolymerization. A complete explanation or mechanism
to fit all known data has not been reported. It is reasonable to say
that the reactivity, the complexation and the steric hindrance of the
comonomers all take part in the alternating tendency, rate, and the ring
size in cyclocopolymerization. The solvent and initiator may also
determine the rate profile of this copolymerization.

Statement of Problem

The objective of the present research has been to study cyclo-
polymerization of donor 1,4-dienes with acceptor monoolefins and hope-
fully learn more about the role of charge transfer complex (CTC) formed
between the comonomers in the cyclocopolymerization mechanism and to

develop a method to elucidate the structure of the cyclocopolymer by
various nuclear megnetic resonance spectroscopic methods. The following
research was conducted with this purpose in mind.

The Structure Analysis of Cyclopolymer of Divinyl Ether-Maleic Anhydride (DVE-MAH) Comonomer Pair.

The ir, H-nmr, and ^{13}C nmr spectroscopies are employed for this well
known 1:2 alternating copolymer. The 100 MHz and 300 MHz H-nmr spectra
were investigated in order to analyze the ring size and hopefully the
cis and trans content of the bicyclic ring. The ^{13}C nmr spectrometer
should give simpler spectra and by comparing with literature values,
it should be possible to determine the ring size of the copolymer.

A partially deuterated divinyl ether (DDVE) was prepared which should
simplify the H-nmr spectral analysis. The 100 MHz and 300 MHz H-nmr
spectra of this DDVE-MAH copolymer should give more information on the
copolymer structure and help in the assignment of the respective signals
of the spectra which has been shown to be informative based on the liter-
ature.[16, 21]

Rate Maximum Analysis

The study of the copolymer rate copolymerization rate as a function
of the feed composition made it possible to determine the participation
of CTC in the cyclocopolymerization. An irradiation at the wavelength
where only complex absorbed should confirm the initiation through CTC.
The participation of CTC in propagation can be supported by an analysis
of the proposed kinetic scheme. In order to compare the rate at the same
light intensity, the quantum yield was measured right after each irradia-
tion. The structure of the cyclocopolymer of divinyl ether-fumaronitrile
monomer pair was determined by elemental analysis and ^{13}C nmr spectroscopy.

CHAPTER II
THE STRUCTURE OF COPOLYMER OF DIVINYL ETHER-MALEIC ANHYDRIDE SYSTEM

Introduction

The field of cyclopolymerization has been explored extensively. A variety of monomers containing two isolated double bonds have been found to polymerize to form linear polymers containing cyclic units and little or no residual unsaturation. High degrees of cyclization are obtained when five- or six-membered rings can form and when all double bonds have the same reactivity such as in diallylquaternary ammonium salts[16] and N-substituted diallylamines.[21] The polymers of N,N-diallyl amines all contained cis and trans-substituted pyrrolidine rings with ratio 5:1. With a substituent on the 2-position such as N-methyl-N,N-bis(2-alkylallyl)-amines, a complex spectra showed the presence of both pyrrolidine and piperidine rings. The ^{13}C nmr spectra of poly(diallyldimethylammonium) chloride showed a predominant content of five-membered ring linked mainly in a 3,4-cis configuration. Several works have studied the polymers obtained from N-substituted dimethacrylamides.[18, 46] In most cases five-membered ring was found predominant with a small amount or no six-membered ring.

The radical cyclization reaction involved in the polymerization has been studied by means of model compounds. Julia reviewed the works on the cyclization of the 5-unsaturated radicals.[47] Without substitution on the radical carbon, only five-membered ring product was obtained. With electronegative substituents on the radical carbon, the six-membered ring product predominated.

Smith studied the cyclization of several 2-(allyloxy)ethyl radicals with tributyltin hydride.[48] The 2-allyloxy ethyl radical gave the tetrahydrofuran derivative as the only cyclic product. The 2-methyl- and 2-phenyl-allyloxyethyl radicals cyclized to give both five- and six-membered ring products; in the latter radical the pyran derivative was the predominant product.

Smith also found that with higher temperature the percentage of the unfavored product increased; this indicated that the ring formation is temperature dependent. It can be concluded that a five-membered ring is energetically favored in the case of symmetrical non-conjugated dienes. A steric effect would change the direction for radical attack on the double bond. For unsymmetrical non-conjugated dienes with opposite polarization on each double bond, the six-membered ring is predominant as explained later. A head to tail cross-propagation has been found for several oppositely polarized vinyl monomer pairs, such as maleic anhydride-vinyl ether pairs,[49] which introduced an alternating copolymer. The cyclocopolymerization of DVE-MAH is similar to unsymmetrical non-conjugated dienes, in which the cyclization step involves a favorable cross-propagation reaction of oppositely polarized units.

It seemed worthwile, therefore, to investigate the structure of the copolymer of DVE-MAH and to study the temperature dependence of the five- and six-membered ring distribution in the copolymer.

Results and Discussion

Synthesis and Copolymerization of Bis(2,2-dideuteriovinyl)ether

Due to the small amount of materials available, the structures of the products in each synthesis step were determined by ir and nmr spectroscopy. A comparison of these spectra with spectra reported in the

literature and the spectra of the corresponding non-deuterated products

prepared by the same procedure confirmed the structures of the deuterated

compounds. In all cases the ir and nmr spectra of the non-deuterated

products were exactly the same as reported in the literature. Therefore,

the procedure for preparation of the non-deuterated ompounds were

applicable for the deuterated analogues.

A reaction scheme is shown in the following route:
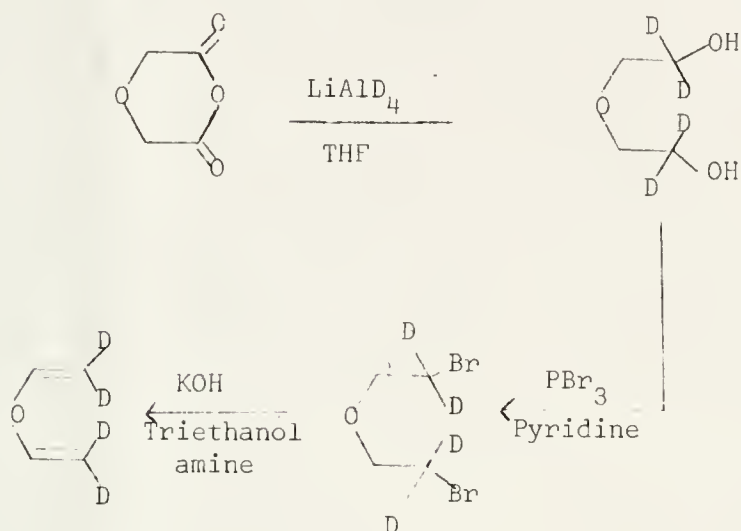
The 2,2,2',2'-tetradeuteriodiethylene glycol was prepared essentially

according to the method given by Bloomfield and Lee with only minor

modification.[50] For complete reduction of anhydride, a prolonged reflux

period was required. In order to take the most advantage of lithium

alluminum tetradeuteride (LiAlD$_4$), only a little excess of the deuteride

was used. The resulting glycol was soluble in water to a large extent,

hence, to isolate it from water solution was difficult. Even a salting

out process did not succeed. The reduction in ether solution was not

successful because of the low solubility of the anhydride. The reaction

seemed not to go at all. The best result was by using tetrahydrofuran

(THF) as solvent, with a small amount of water to destroy the aluminum

salt and release the glycol. The addition of 9 N sulfuric acid to dissolve

the aluminum salt did not improve the yield significantly. Therefore,

the complete dissolution of aluminum salt was not necessary. Water, fol-

lowed by dilute acid was used to bring the glycol into THF solution.

The addition of excess anhydrous potassium carbonate, K_2CO_2, neutralized

the acid by evolution of carbon dioxide and absorbed water present in

the THF solution.

The diethylene glycol prepared by the same procedure showed exactly

the same ir and nmr spectra as reported in the literature. The ir

spectrum of 2,2,2',2'-tetradeuteriodiethylene glycol showed two

absorptions at 2220 and 2110 cm^{-1} of C-D stretching. The structure was

further confirmed by the nmr spectrum, in which a singlet was observed

instead of the multiplet in the spectrum of non-deuterated diethylene

glycol. The peak ratio of 1:2 instead of 1:4 (for diethylene glycol) also

indicated that the product obtained was tetradeuteriodiethylene glycol.

The bromination of deuterated ethylene glycol was straightforward.[51]

The same method when applied to non-deuterated ethylene glycol gave a

product with exactly the same nmr and ir spectra as reported in the

literature. The ir spectrum of the resulting liquid for bis(2-bromo-

2,2-dideuterioethyl)ether showed an absorption at 2170 cm^{-1} which was

assigned to the C-D stretching. The nmr spectrum clearly confirmed the

structure with a singlet at δ 3.80 ppm. On the contrary, non-deuterated

dibromoethyl ether showed an AA'BB' multiplet at δ 3.70 ppm.

Finally the synthesis of bis(2,2-dideuteriovinyl)ether was prepared

by dehydrobromination from the corresponding dibromo compound. Only

the nmr spectrum was analyzed. The disappearance of ABX system which showed up in the spectrum of divinyl ether, was evidence of the replacement of the four terminal hydrogens by deuteriums. A clear spectrum was obtained by using larger sweepwidth. The constants for the hydrogen-deuterium coupling (J_{HD}) was obtained by analyzing this spectrum. By multiplying J_{HD} by 6.5, the corresponding hydrogen coupling constants (J_{HH}) were obtained and were found to be close to the reported value.[52] (Table IV).

Table IV

The Comparison Between J_{HD} and J_{HH}

Coupling	J_{HD} (Hz)	Multiplied by 6.5	Reported J_{HH} (Hz)
trans	2	13.0	13.8
cis	1	6.5	6.2

The synthesized terminal deuterated divinyl ether (DDVE) was copolymerized with MAH at 72°C in cyclohexanone by AIBN initiation. The polymeric product was isolated and purified as a white powdery solid which was soluble in acetone and dimethyl sulfoxide.

A series of copolymers of DVE and MAH were prepared at different temperatures. The ir and nmr spectra were obtained and are discussed in the next section.

The Structure of Copolymer

Infrared (ir) spectra. The ir spectra were shown in Fig. 1. The two strong peaks at 1775 and 1855 cm^{-1} correspond to the reported absorption of succinic anhydride at 1782 and 1865 cm^{-1} [53] for symmetric
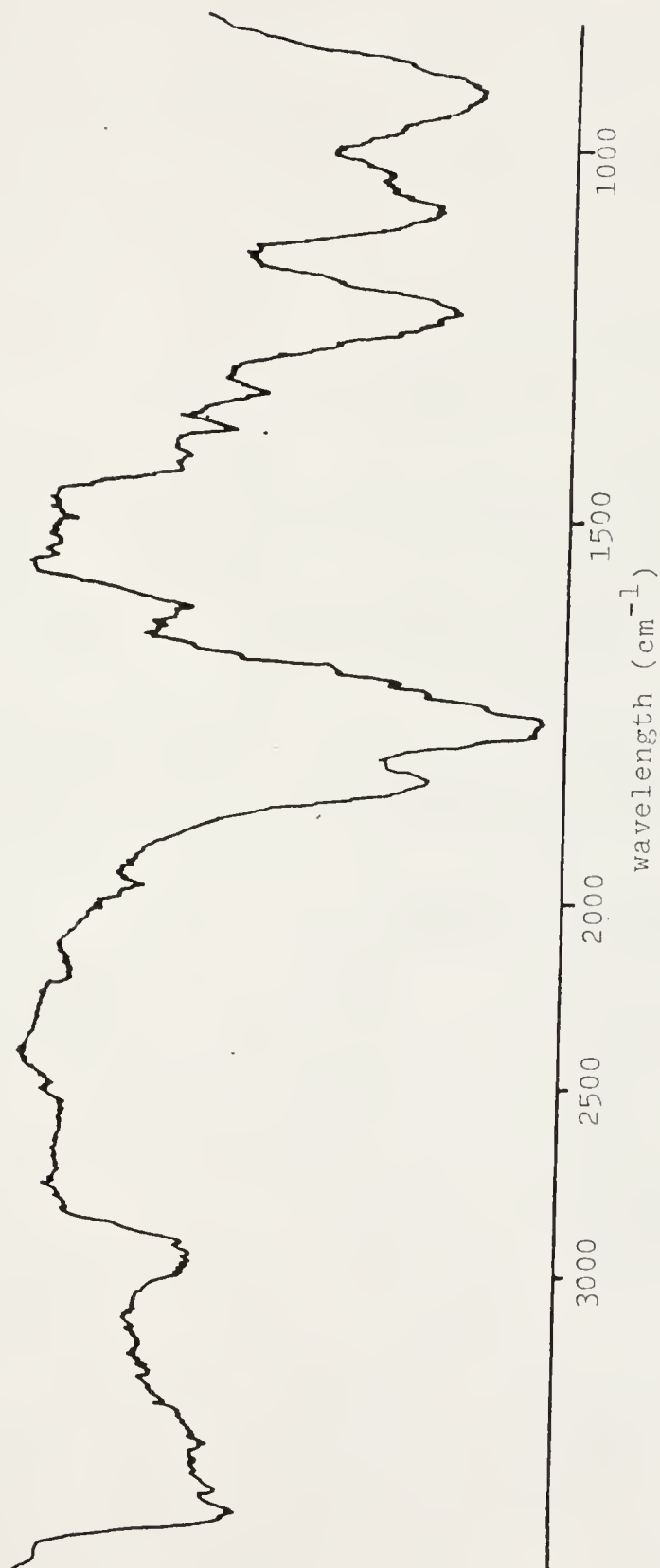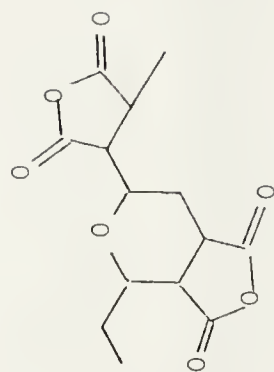
Fig. 1 IR spectrum of the copolymer of DVE-MAH prepared in xylene at 130 °C

and antisymmetric carbonyl stretching, respectively. The strong peaks

at 1230 and 950-920 cm^{-1} were assigned for the C-O-C absorptions for

cyclic anhydride unit. The strong peak at 1090 cm^{-1} with a shoulder

between 1060-1020 cm^{-1} was assigned for the C-O-C stretching for pyran

structure. The five-membered ring structure was ruled out by the fact

that the C-O-C stretching absorption for tetrahydrofuran is at 1062 cm^{-1}.[54]

The structure of the copolymer shown as structure X, with a 2,6-disubsti-

tuted tetrahydropyran ring and an anhydride unit on the 3,4-positions.

X
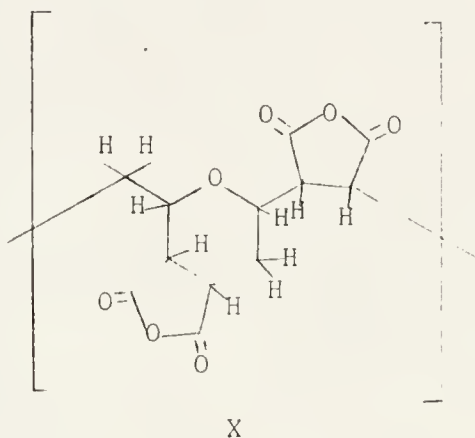
The 1:2 composition of DVE to MAH has been reported by Butler based on

the facts discussed in Chapter I. The spectra for 2,5-disubstituted

tetrahydrofuran has been reported by Mihailovic, et al.[55] They observed

strong absorption at 1100 cm^{-1} .for both cis and trans-2,5-dimethyl-

and diethyltetrahydrofuran.

The structure of the copolymer supported by ir spectra is likely

to have a six-membered ring. A conclusive result cannot be reached

because a suitable model compound for the comparison of ir spectra is

not available.

Hydrogen nuclear magnetic resonance (H-nmr) spectra.

The H-nmr spectra of polymers are usually broad. Therefore,

structure determination by H-nmr spectra is difficult. With the help
of the spectra of deuterated compounds and high resolution nmr spectro-
scopy, it is possible to simplify the spectra and separate the overlapping
peaks. The 60 MHz nmr spectrum for DVE-MAH system copolymer was shown
in Fig. 2a. A four peak pattern was observed at δ 4.49, 4.06, 3.47 and
2.31 ppm with an area ratio of 1:1:1:2. The H-nmr spectrum of the
copolymer prepared with DDVE and MAH under the same polymerization
conditions exhibited the disappearance of the strong peak at δ 2.31 ppm
(Fig. 2b). Only the weak peaks corresponding to the residual solvent
were observed. Hence, the peak in the spectrum of nondeuterated copolymer
at δ 2.31 ppm was assigned for methylene protons which were β to the
ring oxygen. It has been reported that in the spectrum of the copolymer
prepared with DVE-3,4-dideuteromaleic anhydride (DMAH), the two peaks
centered at δ 3.47 and δ 4.06 ppm disappeared.[56] Hence, these two
peaks are due to the four methine protons linked on the anhydride forms.
The peak at lower field was assigned to the proton on the ring, based on
the fact that the proton in a fixed position within a bicyclic ring will
experience a downfield shift caused by the electronegative oxygen nearby.

The methine protons next to oxygen are expected to experience a
deshielding effect to shift to lower field at δ 4.49 ppm. The methine
protons next to oxygen have been reported to absorb between δ 4.00 and
δ 3.30 ppm.[57] Strong electron withdrawing effect of the two succinic
anhydride groups apparently shifts the methine proton to even lower field.

According to this analysis based on peak assignment and area inter-
gration, it can be concluded that the repeating unit of the copolymer has
two to one ratio of maleic anhydride to DVE which are arranged in an
exactly alternating manner. A random distribution of bicyclic and succinic

Fig. 2 60 MHz nuclear magnetic resonance spectra of (a) DVE-MAH copolymer (b) DDVE-MAH copolymer in acetone-d_6

Table V

The Chemical Shifts for the Methine Protons of DVE-MAH Copolymer

Spectra[a]	Next to O	On the Ring Anhydride	On the Backbone Anhydride
60 MHz[b]	4.49	4.06	3.47
60 MHz[c]	4.38-4.44	4.08	3.50
100 MHz[c]	4.18-4.44	3.88	2.96, 3.30
300 MHz[b]	4.29, 4.57	3.92, 4.14	3.01, 3.30
300 MHz[d]	4.34, 4.46		
	4.67, 4.84		
$\Delta\delta$[e]		0.22	0.29-0.34
$\Delta\delta$[f]			0.28-0.47

[a] All chemical shifts (δ) are in terms of ppm relative to the standard, TMS.

[b] Non-deuterated copolymer.

[c] Deuterated copolymer of DDVE and MAH.

[d] Deuterated copolymer of DVE and DMAH.

[e] The chemical shift differences between the assigned cis and trans methine protons.

[f] See reference 59.

anhydride units would give a more complex spectrum than the one reported here.

The 60 MHz H-nmr spectrum is not able to distinguish between the five- and six-membered ring due to the broad peaks caused by vicinal protons and the different conformations and configurations.

For the purpose of distinguishing the cis and trans disubstitutions and the five- and six-membered ring structures, a high resolution 100 MHz H-nmr spectrum was performed for the copolymer of DDVE-MAH in acetone-d_6 at 50°C (Fig. 3). The broad peak at δ 3.50 ppm with a shoulder at δ 3.16 ppm in 60 MHz spectrum was separated into peaks at δ 3.30 and 2.96 ppm. The shoulder between δ 4.38 and 4.44 ppm was still unseparated and broad. A 300 MHz nmr spectrum of DVE-MAH copolymer (Fig 4a) was performed by Butler's group, in which a further separated pattern was observed.[58] The three peaks for methine proton groups are summarized in Table V.

Bode and Brockmann reported that the cis- and trans-2,3-disubstituted succinic anhydride showed 0.47-0.28 ppm difference in chemical shift and the difference decreased with larger substitution.[59] Therefore, we can assign the methine groups of highest field with 0.34-0.29 ppm splitting as the anhydride unit in the copolymer backbone. The one at the lower field with less splitting (0.22 ppm) is then assigned as the anhydride unit on the ring, which is deshielded by the neighboring pyran-oxygen as discussed in the last section. In disubstituted succinic anhydride, the chemical shift for the trans form is less than that for cis form, $\delta_{cis} > \delta_{trans}$, thus the four peaks in the MHz spectra for anhydride protons can be assigned as: 3.01, 3.20, 3.92 and 4.14 for the protons on trans-backbone, cis-backbone, trans-ring and cis-ring anhydride units, respectively. On the backbone, the population of cis anhydride units
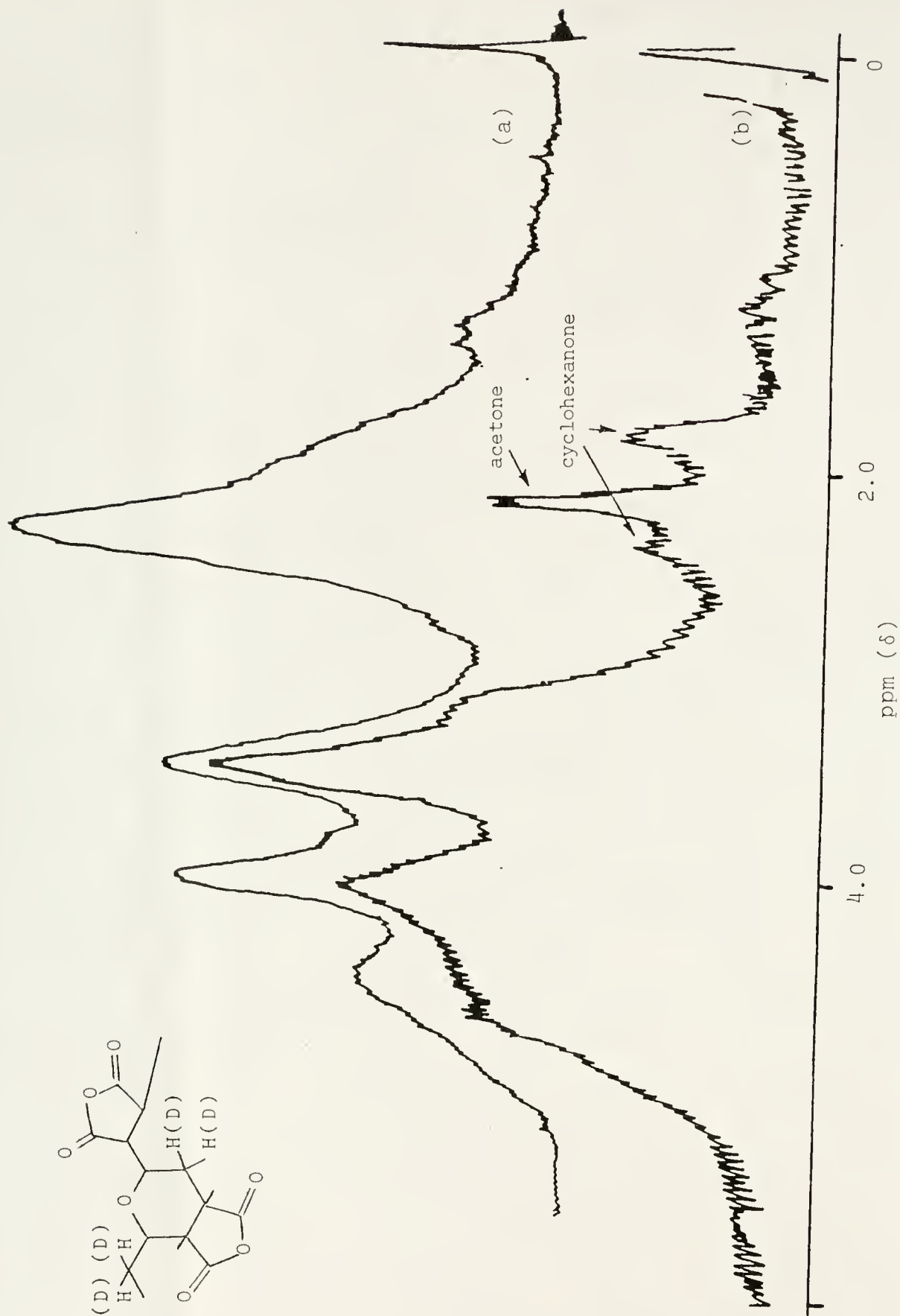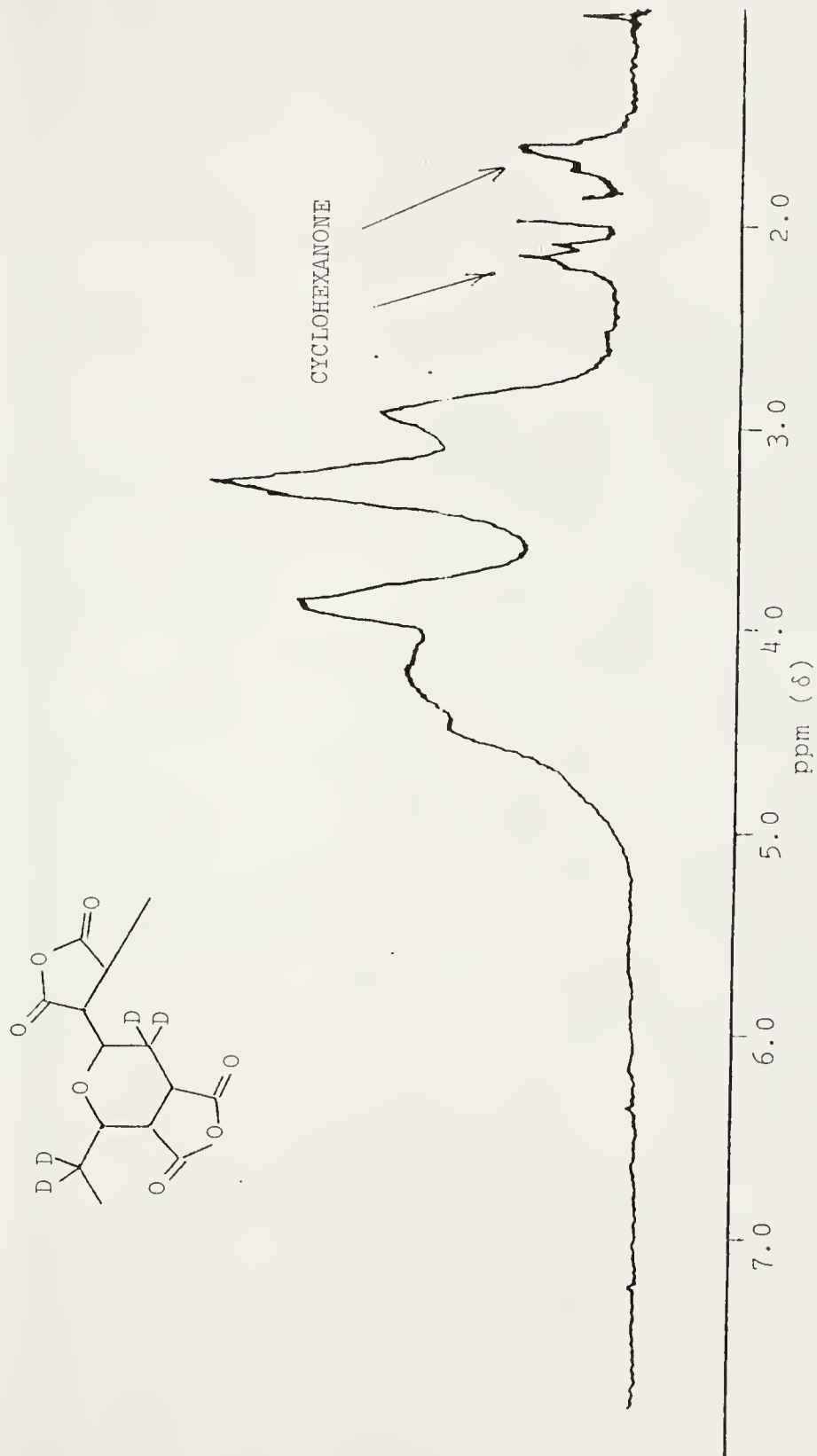
Fig. 3 100 MHz nuclear magenetic resonance spectrum of DDVE-MAH copolymer
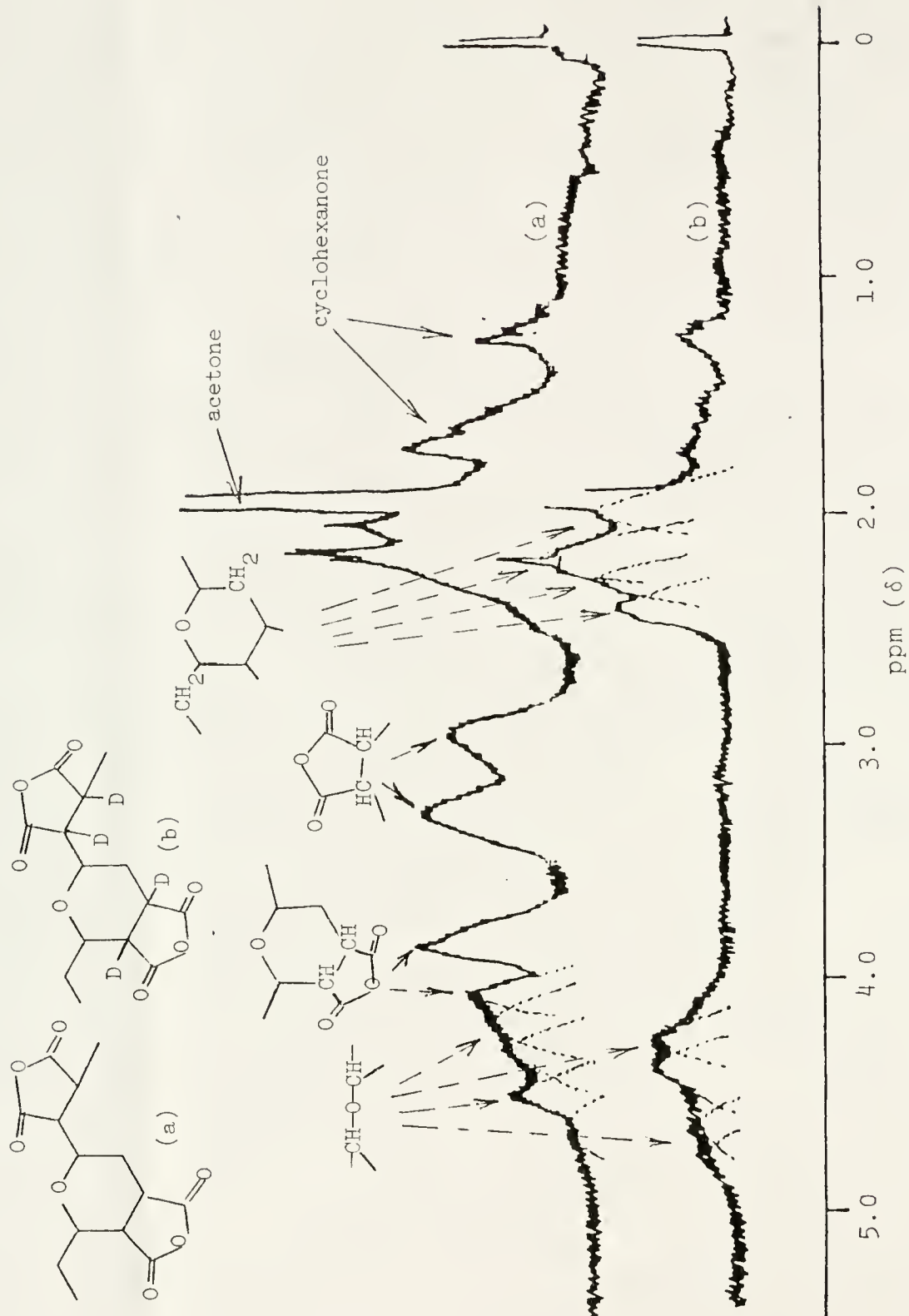
Fig. 4 300 MHz nuclear magnetic resonance spectra of (a) DVE-MAH copolymer (b) DVE-DMAH copolymer in acetone-d_6

and the <u>trans</u> anhydride units are more or less the same. In contrast, more <u>trans</u> form was present in the ring. The latter can be explained by the possible bicyclic ring conformation, where a <u>trans</u> configuration is more favorable. Butler and Guilbault prepared the copolymer of chloromaleic anhydride with DVE having cyclized 1:1 composition with only DVE units in the backbone.[13] They investigated dehydrohalogenation of the copolymer. From the ease with which the copolymer underwent dehydrohalogenation, they suggested that the hydrogen and chlorine atoms on the anhydride unit in the ring were in a <u>trans</u> configuration. However, H-nmr spectra showed the presence of both <u>cis</u> and <u>trans</u> configurations with the latter in favor.

By examination of the model of the bicyclic ring with large substitutions on the carbons next to the oxygen, the six-membered ring with chair form and <u>trans</u> junction is more favorable (<u>trans</u> isomer). In this structure (XI), the two protons at the junction are in <u>trans</u> configuration. A chair form with <u>cis</u> junction is another alternative configuration (cis isomer). However, the latter configuration (XII) experiences more ring strain. On the contrary, a bicyclic ring with two five-membered rings experiences much strain and only cis junction is possible, especially when one of the rings is an anhydride unit (XIII). The heat of combustion of <u>trans</u> bicyclo(3.3.0)octane is greater than the <u>cis</u> isomer by ca. 6 Kcal/mole.[60] Thus, a <u>trans</u> junction pyran bicyclic structure with the presence of <u>cis</u> isomer explains the analysis of 300 MHz nmr spectrum of the DVE-MAH copolymer, based on the analysis of methine protons on the anhydride units.

For a disbustituted cyclic ether, the chemical shift difference between the <u>cis</u> and <u>trans</u> of the methine protons next to oxygen in the

literature have been reported to be between 0.11 and 0.51 ppm.[61, 62,]

In the case of the DVE-MAH copolymer, the methine proton signal was split into two peaks by 0.28 ppm as shown on the 300 MHz spectrum. It is reasonable to assign this group of peaks as a mixture of the two configurations with more trans-isomer present because of the larger area in the higher field corresponding to the cis form which was more populated for a favorable trans isomer.

cis isomer
XII

trans isomer
XI

XIII
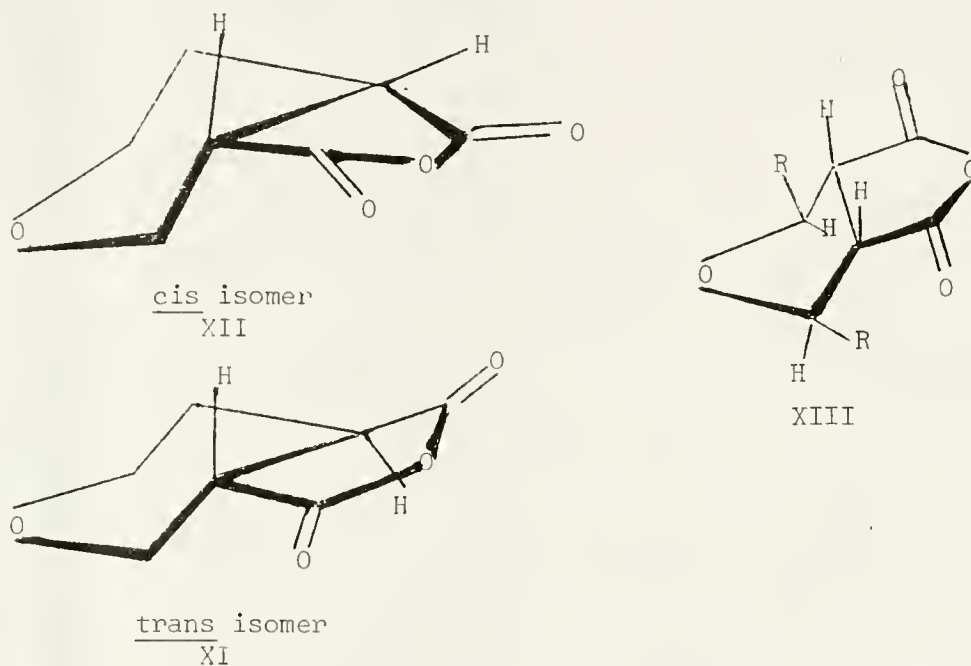
This splitting pattern was more clearly observed in the 300 MHz spectrum for the copolymer of DVE and DMAH (Fig. 4b). The two separated methine proton (next to oxygen) peaks were further split into doublets. The doublet indicated the nonequivalency of the two protons on each side of the oxygen in the pyran ring. In contrast, the two protons for the five-membered ring structure are more or less equivalent.

The methylene peaks on the higher field can be analyzed as a mixture of two doublets; the larger doublet is assigned for trans isomer

which if further split by the fact that the methylene proton groups are not equivalent. The splitting peak at the lower field with less intensity can be assigned to the less populated cis isomer. In fused five-membered ring structure, it is possible that the two methylene groups are linked in either cis or trans configurations.[63] However, a trans configuration would introduce some strain in the bicyclic system with the two bulky substitutions on the pseudo equatorial positions of the half-chair conformation.[64] A cis configuration with the possible conformation is shown in structure XIII.[64] In this structure both the two methine hydrogens and the two methylene groups on the 2- and 5-position are equivalent. Therefore, the splitting on Fig. 4b is most likely due to a chair form six-membered ring with trans junction (trans isomer) with some cis isomer. Further confirmation could be obtained by using bicyclic model compounds and/or studying copolymers of additional monomers, e.g., $CH_2=CDOCD=CH_2$.

^{13}C Nmr Spectra

The line broadening inherent in H-nmr has severely limited the potential of this technique for polymer structure analysis. In contrast, the extended chemical shift range, the absence of significant dipolar line broadening and the simplicity of proton decoupled ^{13}C nmr spectra, in which each carbon resonates as a singlet, makes these spectra extremely useful for the study of polymers.

The spectrum of the copolymer of DVE-MAH was shown in Fig. 5a. The spectrum consists of five major peak groups. From comparison with published data the following general assignments can be made: the broad peaks centered at δ 31.4 ppm with a shoulder at δ 35.8 ppm for methylene carbon, the broad peak centered at δ 44.2 and 51.5 ppm with a shoulder at δ 53.7 ppm for the carbon adjacent to the carbonyl groups, broad peak
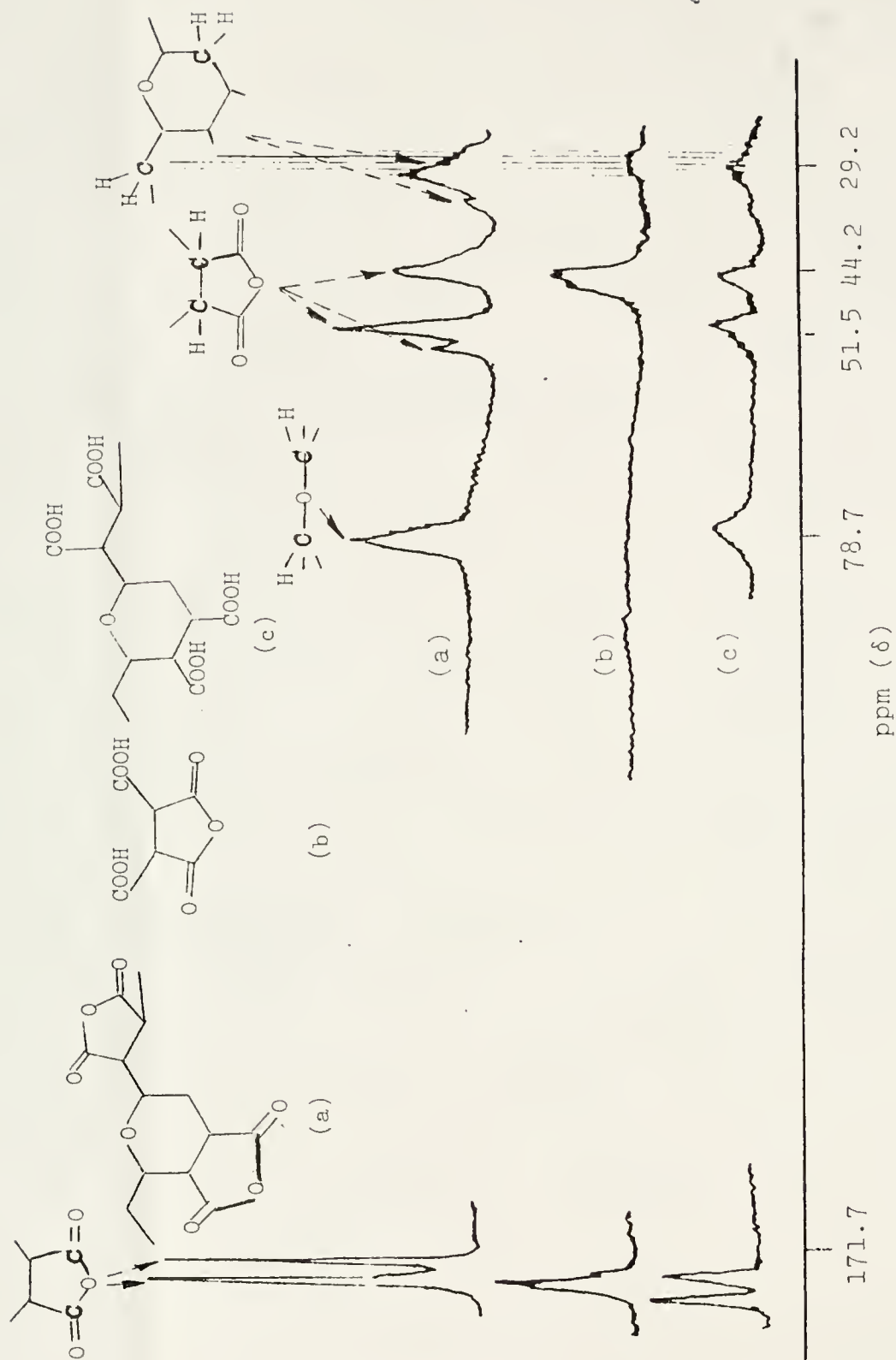
Fig. 5 13C nuclear magnetic resonance spectra of (a) DVE-MAH copolymer (b) poly(maleic anhydride) (c) hydrolyzed DVE-MAH copolymer

centered at δ 78.7 ppm for methine carbon adjacent to the oxygen, the peaks

at δ 171.7 and 174.3 ppm for carbonyl carbons (Fig. 5a). The spectrum for

the copolymer hydrolyzed in D_2O does not change the pattern, but shifts

the peak to lower field (Fig. 5c). A comparison between the hydrolyzed

copolymer and the diacid model compound can be used for the assignment

of spectrum.

In a large series of compounds containing carbonyl groups, the

shielding is mainly influenced by the local electrons on the carbons.

The two carbonyl peaks suggest that two types of carbonyl groups are

present corresponding to the two anhydride carbonyls proposed by H-nmr

apectra, where one of the anhydride units is in the backbone and the other

forms the bicyclic ring. The two carbonyl carbons in each anhydride unit

are not expected to be greatly different from each other as far as the local

electron density is concerned. Therefore, the broadening of the peaks can

be explained either by the two different carbonyl carbons in each anhydride

unit or by the mixing of both cis and trans anhydride forms. A broader

peak is observed at the lower field, which may indicate the equal mixing

of both the cis and trans forms.

The assignment of each carbonyl peak can be made by considering the

chemical shift difference between cis and trans configurations ($\Delta\delta_{cis-trans}$),

which would broaden the carbonyl peaks. The carbonyl carbon absorptions

of succinic anhydrides have been reported to be between δ 171.7 and 175.3

ppm.[65] The ^{13}C nmr spectrum for a dl-meso mixture of 2,3-dimethyl succinic

acid is shown in Fig. 6. The chemical shift differences between the

two carbonyl carbons, the two methine carbons and the two methyl carbons

are 0.7, 0.9 and 1.4 ppm respectively. This small chemical shift differ-

ence for carbonyl carbons between the isomers of dimethyl succinic anhydride
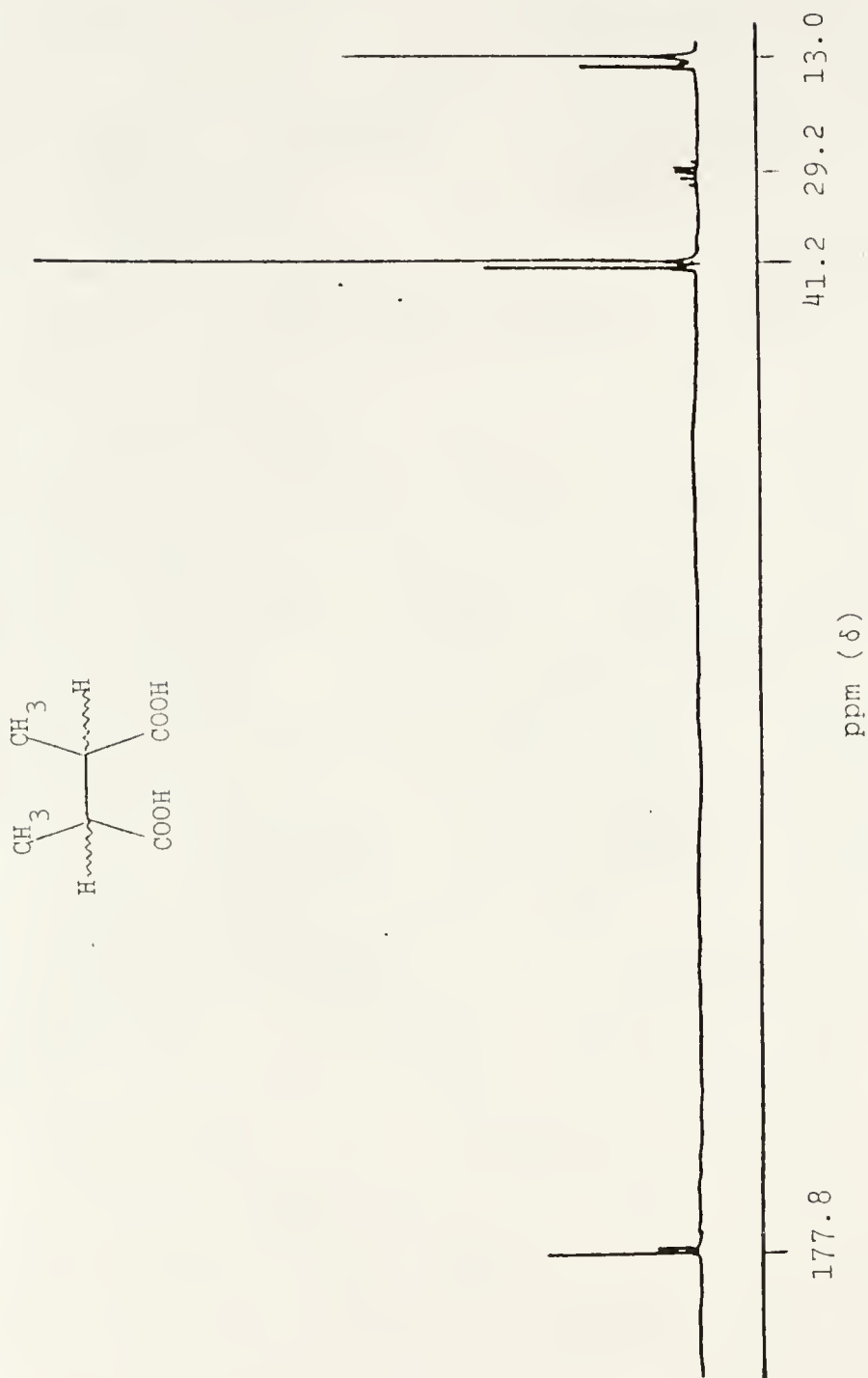
Fig. 6 ^{13}C nuclear magnetic resonance spectrum of 2,3-dimethyl succinic acid

is expected for the carbonyl carbon peaks for the copolymer where only a broadening effect is observed. The peak at the lowest field can be thus assigned for the carbonyl carbons on the backbone because it is broader than the other carbonyl carbon peak. This is reasonable because the sharper peak then assigned for the anhydride on the ring, can be explained by the less population of cis form. This sharper peak is broadened by the hydrolysis of the copolymer as expected by the loss of the rigidity of the bicyclic structure.

A comparison between the spectrum of the copolymer and poly(maleic anhydride)(Fig. 5b)[58] showed clearly that the broader carbonyl carbon peak can be assigned to the anhydride unit on the backbone, and also, the methine carbon peak at the higher field is for the anhydride unit on the backbone. On the other hand, the two peaks at 51.5 and 53.7 ppm with a difference of 2.2 ppm can be assigned for the two non-equivalent methine carbons on the six membered ring by comparing with the β- and γ-carbons on the tetra-hydropyran which has a difference of 2.8 ppm.

The peaks at the lower field of the methine carbon region (δ 51.5-55.5 ppm) are then assigned to the methine carbons on the ring anhydride unit; the larger peak from trans isomer and the weak peak from the smaller contribution of cis isomer. The methylene carbon peak is assigned to the trans isomer which is broadened by the non-equivalency of the two methylene groups in the copolymer. The shoulder at δ 35.8 ppm can be assigned for the methylene carbons of the less populated cis isomer.

By comparing the methine carbons of the copolymer with poly-(diallyldimethylammonium)chloride, (XIV), 1,1,3,5-tetramethylpiperidinium iodide, (XV), and 1,1,3,4-tetramethylpyrrolidinium iodide, (XVI), in Table VI, the chemical shift difference between the cis- and trans-methine carbons in the copolymer is closer to the six-membered ring

structure than the five-membered ring structure.[16]
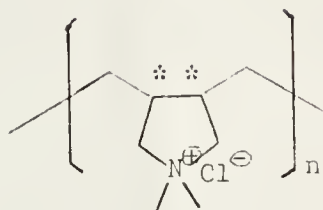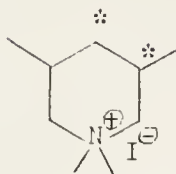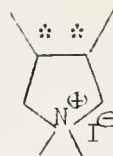
XIV   XV   XVI

Table VI

Chemical Shits Differences Between cis and trans Disubstituted
Vincinal Carbons in ^{13}C nmr Spectra

Structure	$\Delta\delta_{cis-trans}$ (ppm)	
	On the Backbone	On the Ring
Hydrolized Copolymer of DVE-MAH	<1	2.2
2,3-Dimethyl Succinic Acid	0.9	
XIV		4.5-5.0
XV		1.8
XVI		6.2

Kunitake and Tsukino[66] suggested an all five-membered ring structure

for the copolymer of DVE-MAH system by the fact that a highly symmetric

structure is involved, the two singlets observed for the carbonyl carbons

and the comparison of the estimated chemical shift values to the experimental values. This suggestion can be argued against by (1) in the spectrum of the copolymer, the difference between the two carbonyl carbons in each anhydride unit is so small that a splitting causes only the broadening of the peaks. Hence, the absence of the doublet for each peak cannot be explained as the absence of the non-equivalent carbonyl carbons, such as those in the six-membered ring in the copolymer. (2) The analysis of H-nmr spectra was best represented by six-membered ring copolymer structure, although the unlikely mixing of both five- and six-membered ring structures cannot be ruled out completely.

The Temperature Dependence on the Copolymer Structure

Due to the possibility of the mixing of both six- and five-membered ring structures in the copolymer, temperature effect experiments were carried out to investigate the temperature dependence on the contribution of these two structures.

The copolymers were prepared at different temperatures, 25°, 72°, 100°, and 130°C. The results are shown in the experimental section. The spectra for each copolymer are shown in Fig. 7. No major change was observed. The small side peak at δ 35.8 and 51.5 ppm both gradually disappeared or flattened with the decreasing of temperature. This small change cannot be considered to be real because of the accidental experimental errors such as lower resolution and the different concentrations of the samples. Even the different solvents used for preparation should be considered.

It is reasonable to conclude that no significant change of structure caused by the temperature effect is obtained. This fact can be explained

Fig. 7 ^{13}C nuclear magnetic resonance spectra of DVE
MAH copolymer prepared at (a) 130, (b) 100, (c) 72,
(d) 25 °C

by the production of only one energetically favored product which is
the six-membered ring structure as revealed by all the spectroscopic
analysis.

The Mechanism of Cyclization

The structure and temperature analysis concluded that a highly
energetically favored six-membered ring copolymer was the product of
the copolymerization of DVE-MAH system. In cyclization of the sym-
metric non-conjugated dienes, the ring size is controlled by the
entropy effect of the two ring formation processes. A five-membered
ring product is favored because of the less entropy change involved.
With substitution, a sterically favored six-membered ring formation
is able to compete with the former process. Also, the substitution on
the radical carbon of the uncyclized radical makes both the processes
higher activiation energies and hence, less selective. At the extreme,
with two electronegative and steric substituents on the radical carbon,
a six-membered ring formation will be highly favored.[47]

The energetical factor is much different for a cyclization involving
non-symmetric non-conjugated dienes such as the cyclization in the
cyclocopolymerization of DVE-MAH system. During the cyclization step,
the vinyloxy double bond is attacked by a radical on the anhydride unit:

XVII
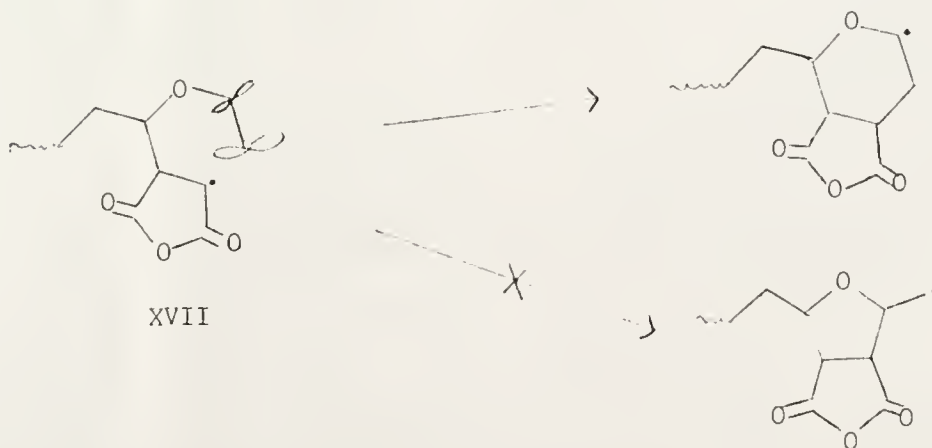
This process can be shown to be highly enthalpy-controlled by considering the closer energy gap between the HOMO of vinyloxy double bond and the singly occupied molecular orbital (SOMO) of the anhydride radical than that for the corresponding symmetrical diene cyclization.
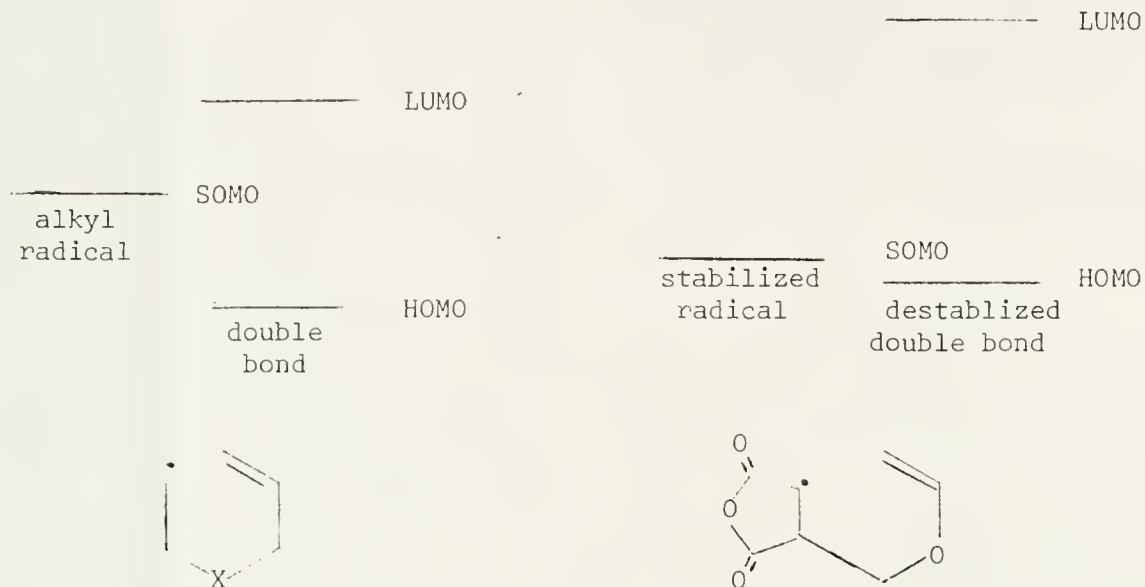
The HOMO of the vinyloxy double bond is polarized to have higher orbital density on the terminal position.[67] Therefore, a fast radical addition on the terminal carbon of the double bond leads to a six-membered ring radical. A copolymer with six-membered ring structure X is thus obtained.

As discussed in chapter I, a charge transfer complex was proposed to explain the fast cyclization. The charge transfer complex can be applied here with the help of HOMO-LUMO concept to predict the ring structure of the cyclization step.

The Milliken theory of overlapping and orientation principle predicts that stabilization in the molecular complex formation should essentially

be determined by the overlap of the donor HOMO and the acceptor LUMO.[68]
In the examination of ir and Raman spectra of DVE, Claugue and Danti
proposed the presence of two rotational isomers.[69] The more stable isomer
has C_s symmetry, in which the two vinyl groups, although coplanar are
non-equivalent. Hirose and Curl examined the microwave spectrum and
assigned the C_s conformer.[70] They found a small nonplanarity caused
by H-H repulsion between the β-hydrogen of the cis vinyl group and the
α-hydrogen of the trans vinyl group. (XVIII).

XVIII

cis-trans
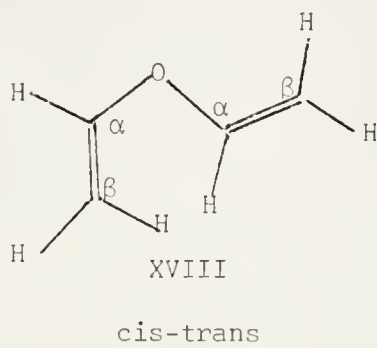
The charge distributions in vinyl ether and vinyl methyl ether were
calculated by CNDO/2 method by Fueno, et al.[67] It was found that a large
electron density was on the terminal position as in sturctures XIX and
XX.

XIX

XX
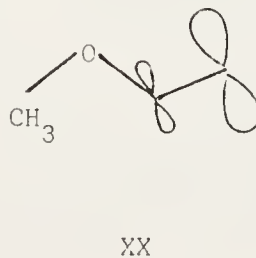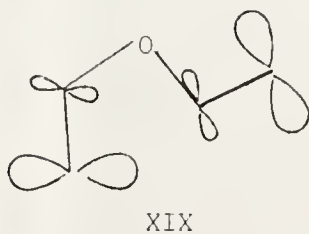
This charge density of orbital actually describes the orbital density of the HOMO of DVE. The LUMO of MAH has been described by Fukui as structure XXI with higher orbital densities on the double bond carbons, but antisymmetrical to the plane of symmetry of this compound.[71]

Therefore the most stable conformation for a DVE-MAH complex can be expected as XXII, based on the conformer structure of DVE and the molecular densities of both comonomers.
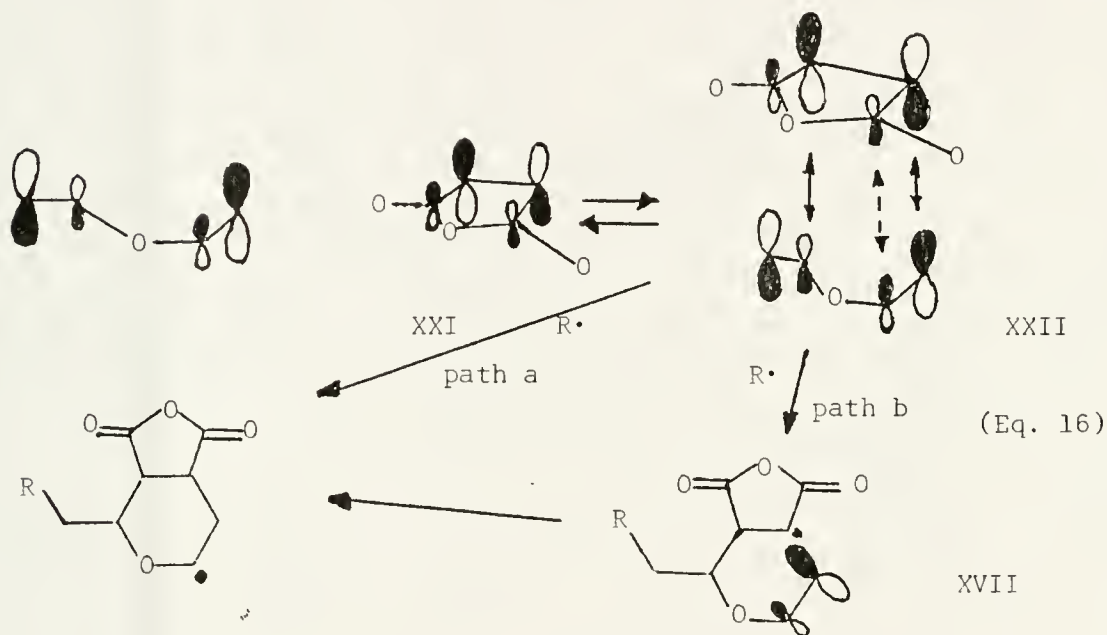
When this complex is initiated by a radical, a six-membered ring radical will be formed concerted (Path a) or stepwise through an anhydride radical addition on the terminal carbon of the vinyloxy unit (path b). This complexation would reduce the energy gap between the complex and the propagating anhydride radical, thus, a radical addition on the complex occurred and the reaction is supposed to be fast. This special

complexation and/or interaction would significantly reduce the activation enthalpy for the formation of six-membered ring. In the range of the temperature sutdied, a five-membered ring formation cannot compete with it at all, which explains the temperature independence on the structure of the cyclocopolymerization.

In conclusion, on the mechanism of the cyclization and copolymerization of DVE-MAH system, it is reasonable to be stated as follows.

(1) The intramolecular cyclization is favored over the intermolecular addition due to the lower entropy change of the former process than the latter one. This explains the high degree of cyclization.

(2) The entropy preference cannot be explained on the base of activation energies and the statistical probability. A preorientation either through the delocalization of the radical with the intramolecular double bond or the formation of complex is proposed.

(3) This preorientation would lead to a six-membered ring structure by a favorable energy factor based on the HOMO orbital density of DVE. For a symmetrical nonconjugated diene the five-membered ring cyclization is favored by the entropy factor.

(4) A faster rate of this cyclocopolymerization than the copolymerization of the corresponding monoolefin pairs can be explained by the closer energy of the anhydride radical to the complex.

The proposed cyclization mechanism can be applied on other comonomer pairs and is worthy of further investigation.

CHAPTER III
THE COPOLYMERIZATION OF DIVINYL ETHER-FUMARONITRILE

Introduction

It was pointed out in Chapter 1 that a donor-acceptor pair of
comonomers could produce alternating copolymer through a charge transfer
complex (CTC). In the cyclocopolymerization of donor 1,4-dienes with
acceptor monoolefins, alternating cyclocopolymers having 1:2 composi-
tion were obtained for several systems. The participation of CTC formed
between the donor and acceptor was proposed to explain the alternating
copolymerization. However, it has been known for sometime that the
compositions for the copolymers are 1:2 while the stoichiometry of the
CTC are always 1:1. An alternating copolymerization of a CTC and a free
monoolefin was proposed as an explanation. It has been shown that
when an acceptor monoolefin is highly sterically hindered and hence much
less reactive, according to the above explanation, a 1:1 cyclocopolymer
was obtained apparently through the homopolymerization of CTC.[14], [43]
With a less sterically hindered monoolefin and less reactive monoolefin
it is possible to form a cyclocopolymer with composition between 1:1
and 1:2. The cyclocopolymer of DVE-FN has been reported having the FN
content between 0.55 and 0.63 mole fraction which is in the range of
0.50-0.67 for the 1:1 and 1:2 composition.[32] With dilution, less FN
content was reported and a contribution of either homopolymer structure
of DVE and/or 1:1 comonomer unit in addition to the regular 1:2
comonomer unit was proposed as an explanation.[37]

A further structural analysis and the study of the participation of CTC in the copolymerization are discussed in this chapter

Results and Discussion

Study of the DVE-FN complex in Acetonitrile

On the basis that the complex formed between DVE and FN may participate in the mechanism of initiation of the photocopolymerization in acetonitrile solution, the characteristics of the complex were studied in the same solvent. The existence of the complex was established by UV spectrophotometry. A mixture of 0.6 m/l of DVE and 0.6 m/l of FN showed a large absorption between 250 nm and 350 nm (Fig. 8) although a distinguishable new absorption band was not observed. This large enhancement of absorption indicated the presence of complex. A 1:1 stoichiometry was determined by the continuous variation method at 300 nm.[72] (Fig. 9). The maximum of the absorption for different compositions of DVE and FN, while their total concentration was kept constant was found for equimolar composition.

The charge transfer complex of an acceptor-donor pair is in equilibrium with the free components. The charge transfer complex exists in resonance between the no-bond state and the dative state; thus the wave function of the charge transfer complex (Ψ_{CT}) can be expressed as a linear combination of wave functions of the no bond state [$\Psi(D,A)$] and the dative [$\Psi(A^{\overline{\cdot}}, D^{\overset{+}{\cdot}})$] (Equation 1 and 2).

$$A + D \underset{\longleftarrow}{\overset{K_c}{\longrightarrow}} \quad [(A,D) + (A^{\overline{\cdot}}, D^{\overset{+}{\cdot}})] \qquad (\text{Eq. 17})$$
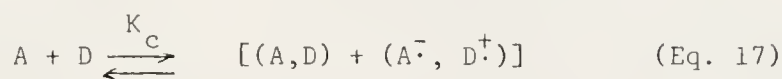
$$\Psi_{CT} \simeq a\Psi \cdot (A,D) + b\Psi \cdot (A^{\overline{\cdot}}, D^{\overset{+}{\cdot}}) \qquad (\text{Eq. 18})$$
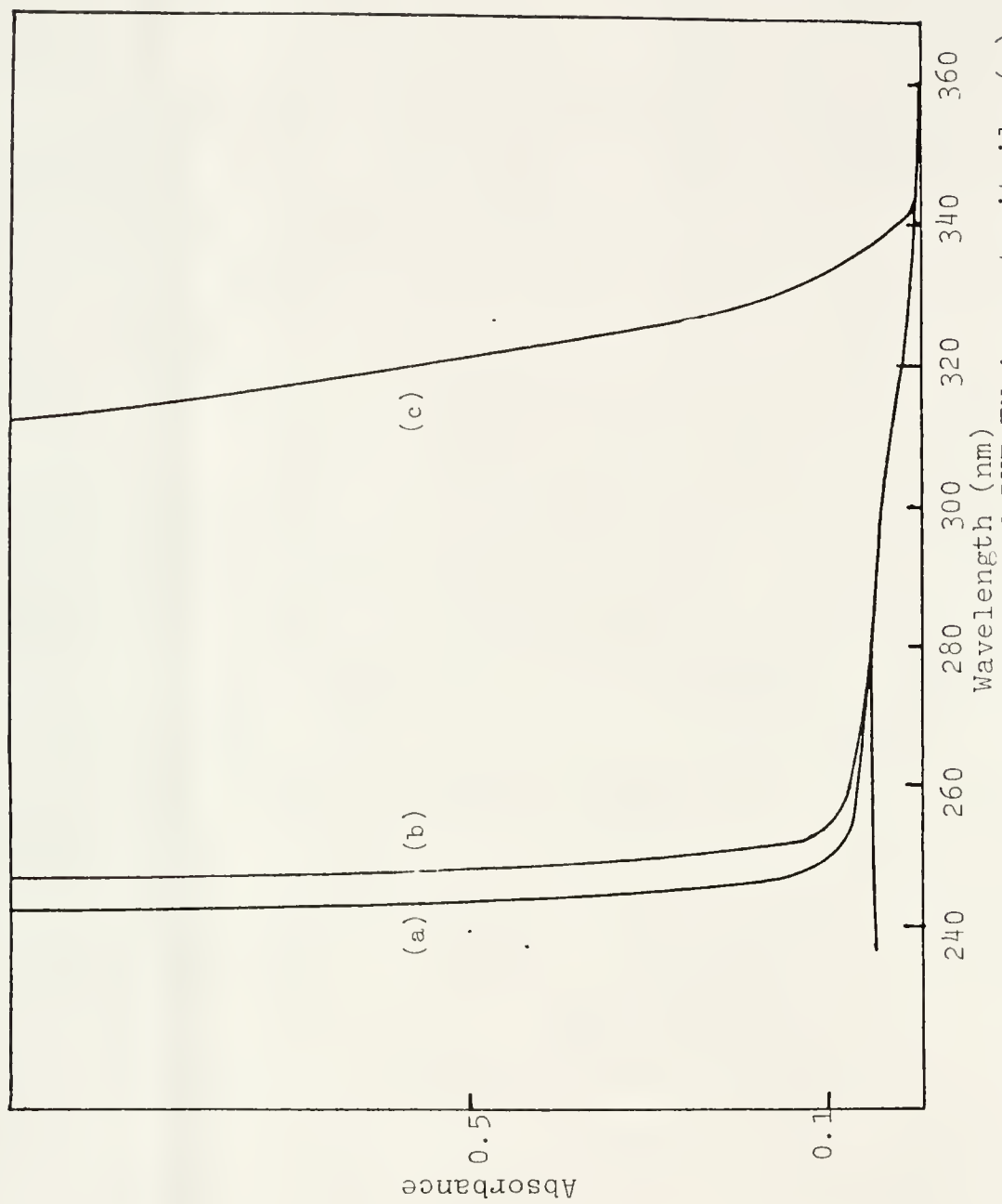
Fig. 8 The absorption of the complex of DVE-FN in acetonitrile (a)
0.6 m/1 of DVE, (b) 0.6 m/1 of FN, (c) (DVE) = (FN) = 0.6 m/1.
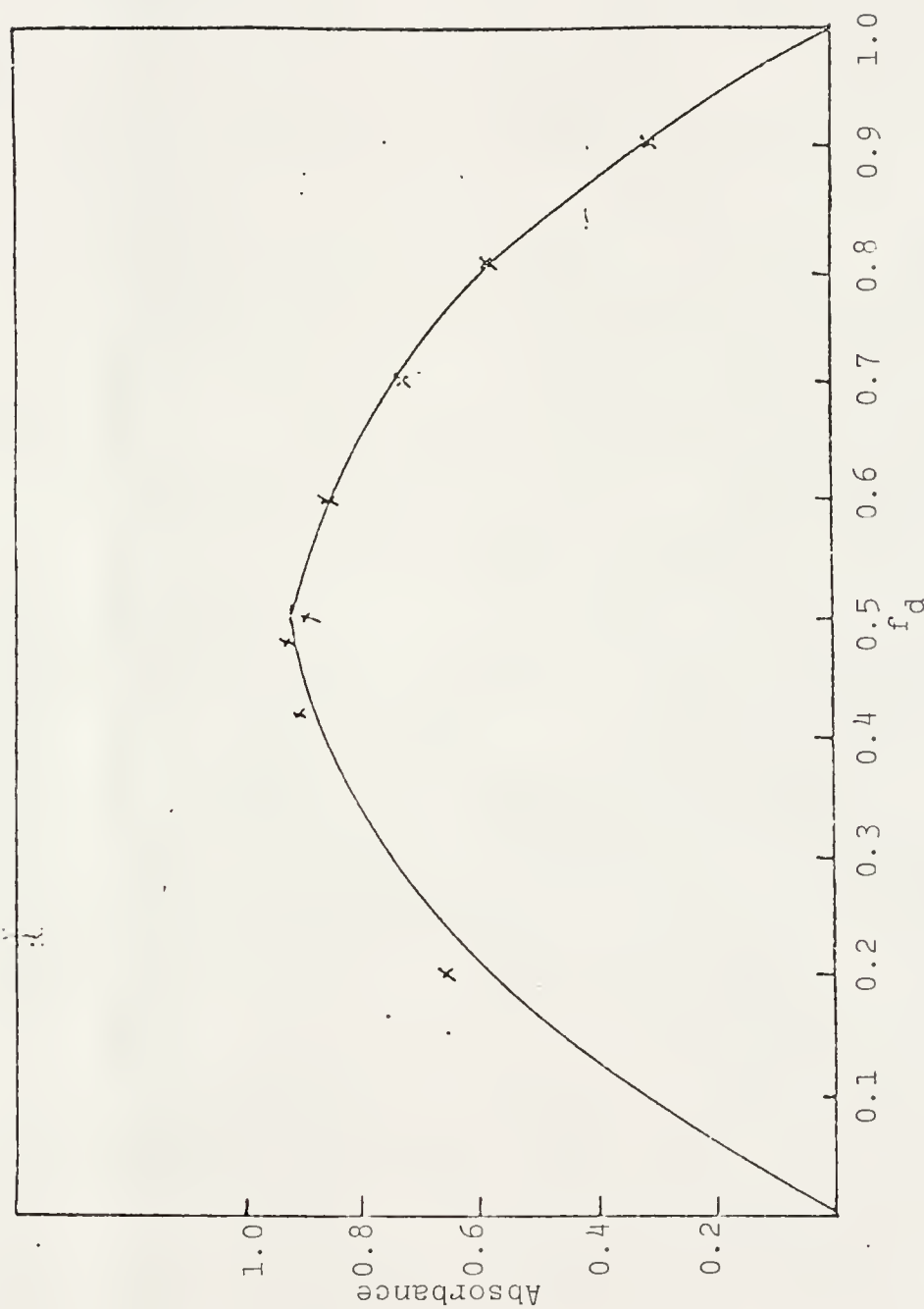
Fig. 9 The determination of the stoichiometry of the DVE-FN complex in acetonitrile by continuous variation method at 300 nm (DVE) + (FN) = 0.60 ± 0.03 m/l

For a regular loose complex, $a^2 >> b^2$ in the ground state of the complex. The dative structure corresponds to an ionic-radical-like pair. There must be also an excited state (Ψ_{CT}^{*}) which can be called a charge transfer state[73] given by

$$\Psi_{CT}^{*} \simeq b^{*}\Psi_o(A,D) + a^{*}\Psi,(A\overline{\cdot},D\overset{+}{\cdot}) \qquad (Eq.\ 19)$$

The excited state is mostly dative ($a^{*2} >> b^{*2}$); excitation of an electron from Ψ_{CT} to Ψ_{CT}^{*} essentially amounts to the transfer of an electron from donor to acceptor. Spectroscopic absorption would occur with this excitation (charge transfer absorption). A charge transfer absorption is possible for any pair of molecules if in contact, even if they do not form a stable complex.

A complete absorption spectrum of a complex consists of absorption to (1) locally excited state (states of donor or of acceptor, more or less but usually not greatly modified in the complex.) (2) charge transfer states [(Ψ_{CT}^{*} in Eq. 19, and other charge transfer states including the excited dative structures, for example $\Psi(D\overset{+}{\cdot}^{*},A\overline{\cdot})$].

The equilibrium constant (K_c) of the complex can be measured by using Merrifield and Phillips method.[74]

$$\frac{A_{\lambda c}}{(D)_o} = -K_c A_{\lambda c} + K_c(A)_o \varepsilon_{\lambda c} \qquad (Eq.\ 20)$$

$(D)_o$ = The initial donor concentration

$(A)_o$ = The initial acceptor concentration

$A_{\lambda c}$ = Absorbance of complex at certain wavelength

K_c = The equilibrium constant for the formation of weak complex

$\simeq$ (Complex)/(D)(A)

$\varepsilon_{\lambda C}$ = The extinction coefficient of the complex at wavelength.

For a series of solutions containing different concentrations of DVE but with constant concentration of FN, with condition (DVE)>>(FN), a plot $A_{\lambda C}$/(DVE) against $A_{\lambda C}$ should be linear. From the gradient of the line, K_C may be evaluated directly without recourse to an extrapolated intercept. The absorption of DVE-FN complex and the resulting plot in acetonitrile are shown in Fig. 10 and Table VII. The equilibrium constant was small (K = 0.10) and cannot be evaluated exactly, but it is compatible with the equilibrium constant measured in methanol solution $(K_C = 0.12$ to $0.20)$.[39]

Table VII

Determination of Equilibrium Constant of FN-DVE in
Acetonitrile with Constant FN Concentration (0.00101 m/1)

$(D)_0$	280 nm		300 nm	
m/c	A	$A/(D)_0$	A	$A/(D)_0$
0.846	0.031	0.0520	0.013	0.0154
1.69	0.081	0.0479	0.029	0.0172
2.12	0.100	0.0472	0.031	0.0146
2.96	0.137	0.0463	0.042	0.0142
3.81	0.152	0.0399	0.040	0.0105
K_C	0.09		0.11	

The equilibrium constant of complexation can be determined by nmr spectroscopy using the Hanna-Ashbaugh equation.[75] The attempted nmr method failed because one of the quartet absorptions of the α-vinyl
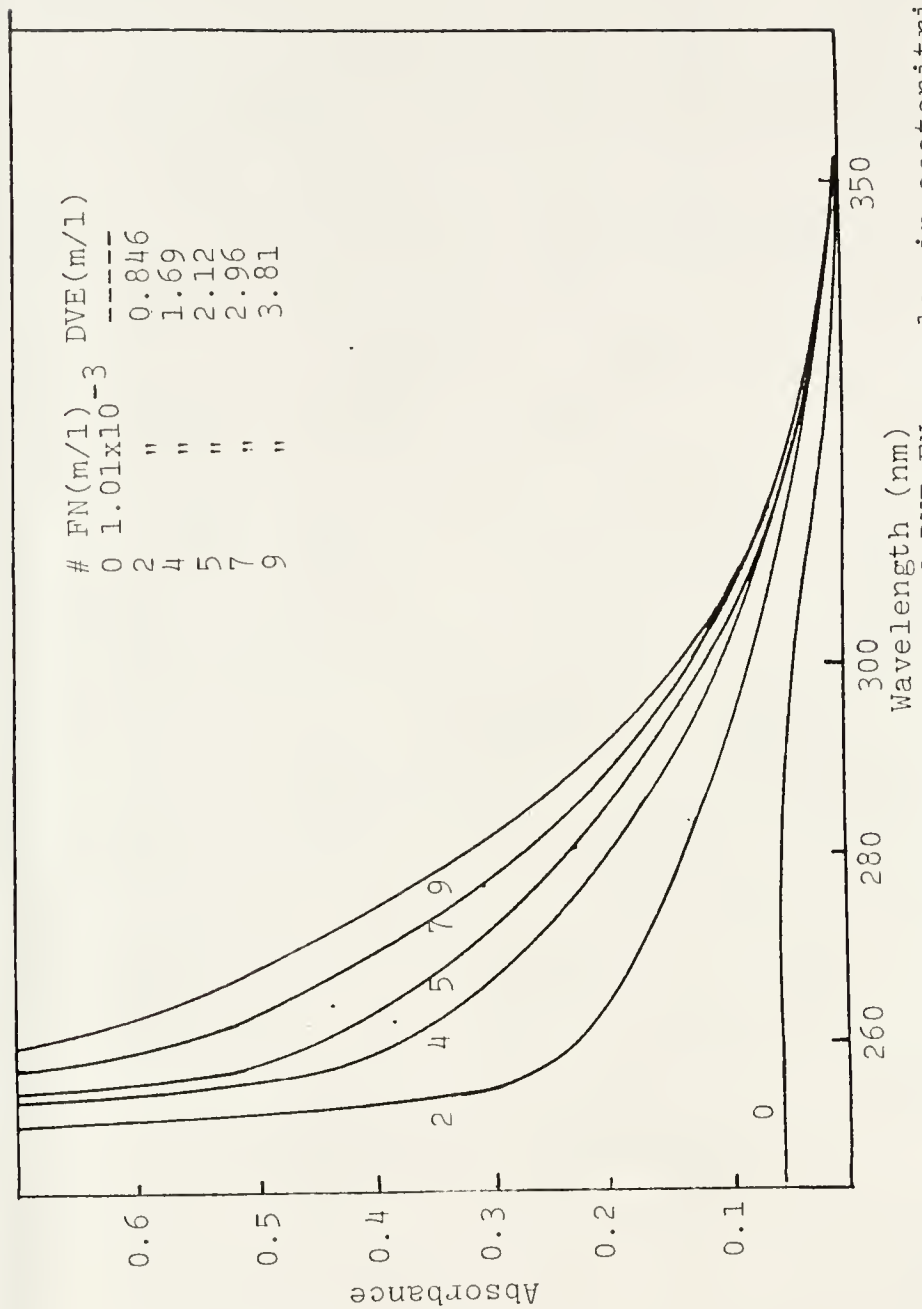
Fig. 10 Charge transfer absorption of DVE-FN complex in acetonitrile

proton of DVE covered the peak of the protons of FN, whose chemical shift was to be used to determine the equilibrium constant in acetonitrile.

The Structure of the Complex

The spectroscopic determination of stoichiometry and the equilibrium constant of the charge transfer complexes of monoolefins with 1,4-dienes have been thoroughly discussed previously.[37] Amazingly, in all cases studied the stoichiometry is 1:1. The structure of the complex has not been established. Either one or both of the double bonds of the 1,4-diene can be complexed with acceptor. Take DVE and FN as an example:
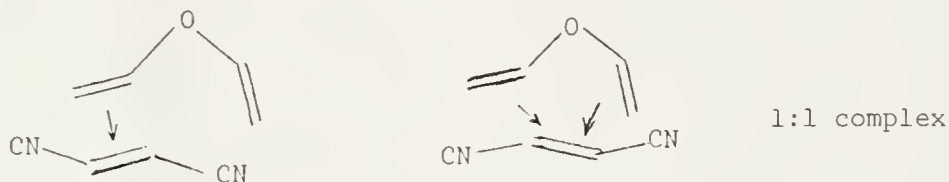
1:1 complex

The first structure is not likely because with a free double bond available, a second acceptor would be complexed more or less as easily as the first acceptor molecule to form a 1:2 complex.
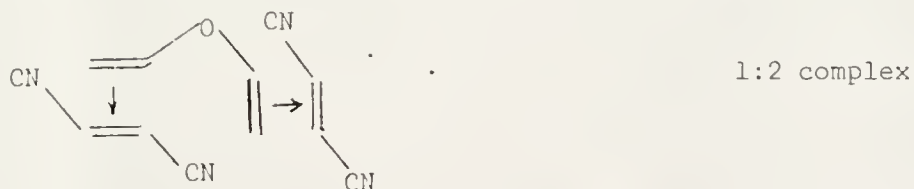
1:2 complex

As pointed out in Chapter II, considering the conformation of DVE and the orbital densities of both HOMO of DVE and LUMO of acceptor, the most stable conformation of the complex can be predicted as structure XXIII. The proposed relation between no bond state and the dative state of this complex is shown in equation 21.

XXIII

Dative state   No bond state   (Eq. 21)
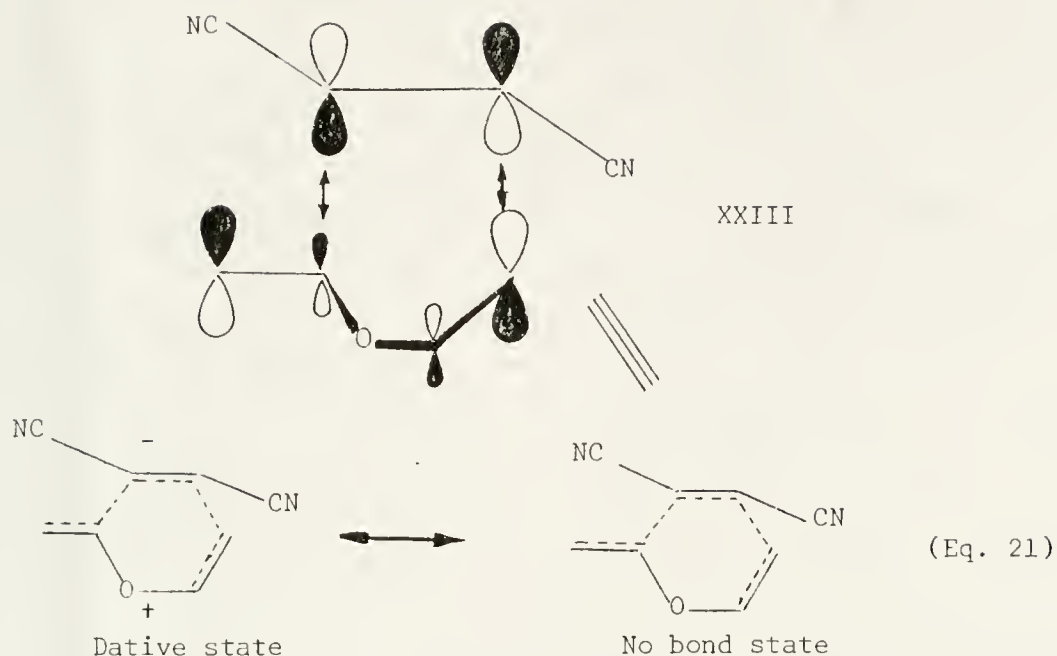
At ground state the complex can be represented by the no bond state, the excited state (CTC)* after the absorption of appropriate light energy, can be represented by dative state. In general an excited state would be radiationlessly deactivated without associating with external environment. In the case of (CTC)*, the state is so polar that the environmental polar molecules (acceptor, donor and ground state complex) would participate in its deactivation processes.

At 236 nm, while most of the light is absorbed by the free monomers to form excited monomers, the excited state of DVE would interact with the ground state of FN to form an exciplex which possesses higher energy than the previously mentioned c rge transfer state [(CTC)* formed by irradiation at 300 nm where only the complex absorbs].[76] The exciplex is polar enough to be deactivated with the participation of ground state molecules. (Scheme I)

$(DVE \longrightarrow FN) \xrightarrow{300 \ nm} (DVE \longrightarrow FN)^{*} \xrightarrow[\text{molecules}]{\text{environmental}} DVE + FN$

$DVE \xrightarrow{236 \ nm} DVE^{*} \xrightarrow{FN} (DVE^{*} \rightarrow FN) \xrightarrow[\text{molecules}]{\text{environmental}} DVE + FN$

environmental
molecules

DVE
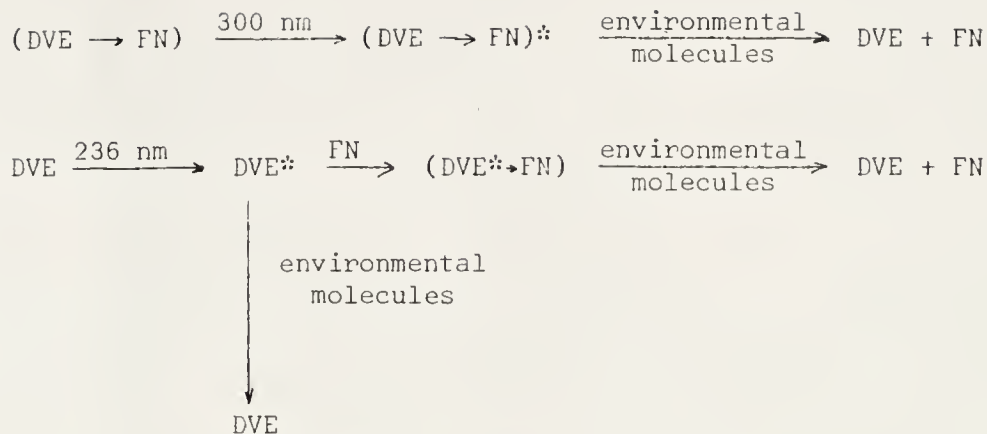
Scheme I

The Structure of the Copolymer of DVE-FN System

Ir and H-nmr spectra. The ir, H-nmr and ^{13}C nmr spectra were record-ed for the copolymers prepared by irradiation at 300 nm, 236 nm and with AIBN, in acetonitrile with feed composition f_d = 0.5 (Table VIII).

Table VIII

Comparison of Copolymers Initiated by Different
Methods in Acetonitrile

Feed Composition		Initiation	Conversion	m_d*
(FN)	(DVE)			
0.6 m/l	0.6 m/l	AIBN	44%	0.408
0.6 m/l	0.6 m/l	236 nm	40%	0.402
0.6 m/l	0.6 m/l	300 nm	55%	0.486

*Molar fraction of DVE in copolymer calculated from nitrogen
and carbon content

All the copolymers showed the same characteristics in ir and H-nmr spectra, thus indicating that the same propagation processes are employed for all methods of initiation.

The copolymers absorbed in the infrared region: 2250 cm^{-1} (s) (CN stretching) and near 1100 cm^{-1} (broad)(ether group), showning the existence of the comonomer units. There was also the presence of vinyloxy double bond absorption at 1630 cm^{-1}. It has been observed[32] that only a small amount of residual unsaturation (from 2.0 to 3.5%) was in the copolymer prepared by the initiation of AIBN in dimethylformamide. The infrared spectra of copolymers initiated by light at both 236 nm and 300 nm had the same characteristics as the one initiated by AIBN in acetonitrile (Fig. 11). It is reasonable to assume that the same small amount of unsaturation was in the photocopolymers. This conclusion was also shown in the H-nmr spectra (Fig. 12) where no absorption contributed by vinyloxy double bond was observed. Therefore, there is no significant contribution of the structures with the pendant vinyl group in the copolymer.

XXIV
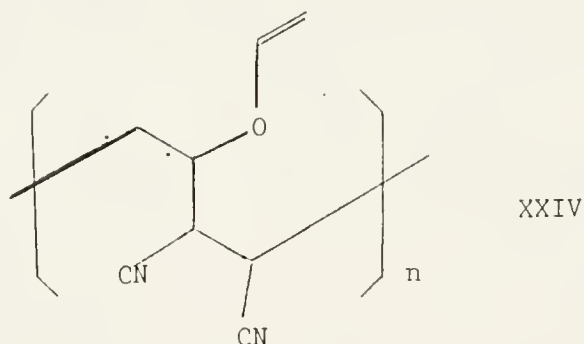
The composition of the copolymer. The composition of the copolymers has been determined over a wide range of monomer feed compositions. The copolymers of DVE-FN are quite hygroscopic. The elemental analysis showed higher hydrogen and oxygen weight percentages than calculated from nitrogen
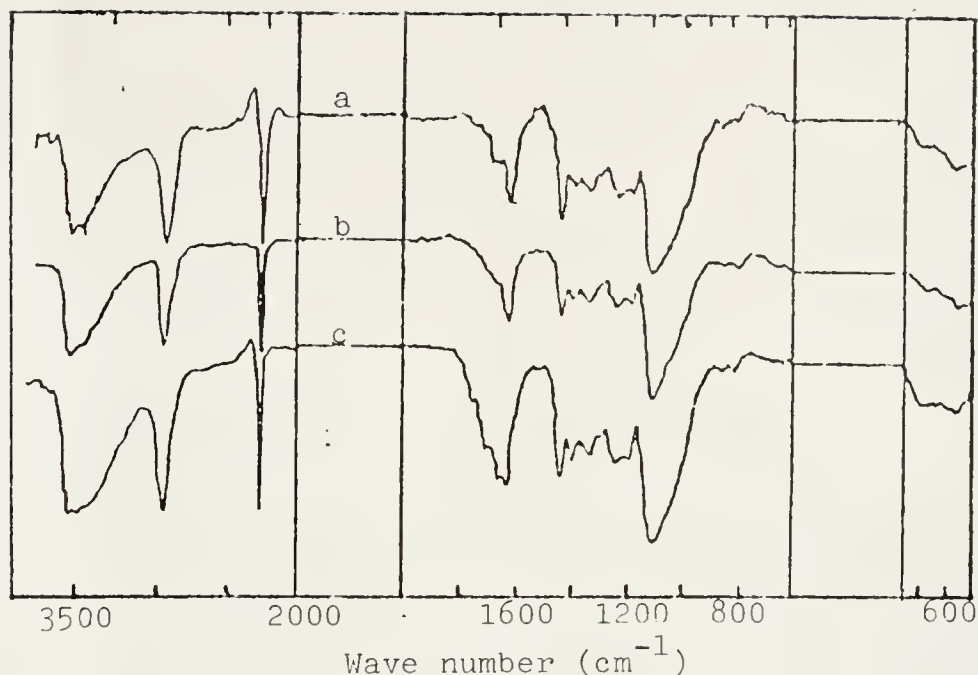
Fig. 11 IR spectra of the DVE-FN copolymer initiated
(a) at 300 nm, (b) at 236 nm, (c) by AIBN.
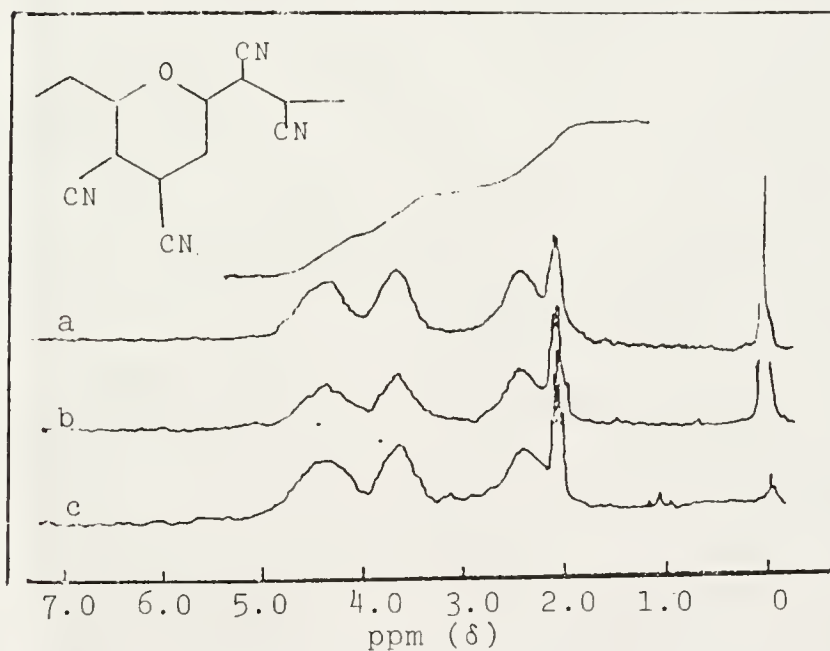
Fig. 12 60 MHz nuclear magnetic resonance
spectra of the DVE-FN copolymer initiated
(a) at 300 nm, (b) at 236 nm, (c) by AIBN

and carbon.   The nitrogen content is only from FN monomer, the calculation
of the number of nitrogen atoms permitted the determination of the
copolymer composition.

no. of moles of FN = no. of moles of nitrogen atoms/2

$$\text{no. of moles of DVE} = \frac{\text{no. of moles of carbon atoms - no. of moles of FN} \times 4}{4}$$

m_d = the molar fraction of DVE in the copolymer

$$= \frac{\text{no. of moles of FN}}{\text{no. of moles of DVE + no. of moles of FN}}$$

The results are shown in Table IX and Fig. 13.

Table IX

The Compositions of Copolymers Prepared in Acetonitrile at
Room Temperature within 10% Conversion

Concentration (m/l)			300 mn	236 nm
(FN)	(DVE)	f_d^b	m_d^c	m_d
0.4	1.6	0.80	0.410	0.408
0.8	1.2	0.60	0.372	0.436
0.6	0.6	0.50	0.486[a]	0.402[a]
1.2	0.8	0.40	0.412	0.400
1.6	0.4	0.20	0.351	0.436
Average			0.406	0.416

[a] More than 40% conversion.
[b] Molar fraction of DVE in feed.
[c] Molar fraction of DVE in copolymer calculated from
   nitrogen and carbon weight percentage.
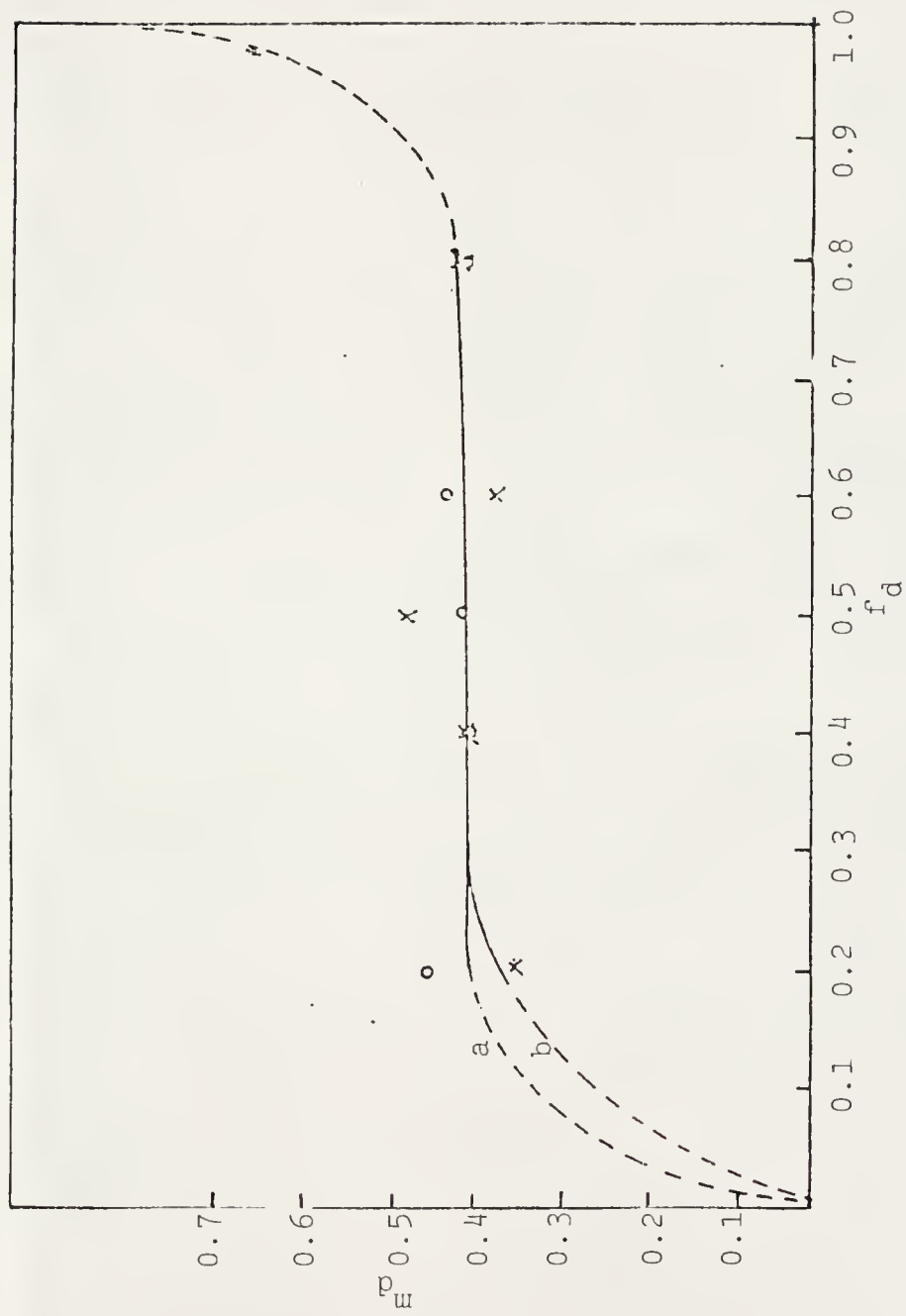
Fig. 13 The compositions of the DVE-FN copolymer initiated at (a) at 236 nm, (b) at 300 nm.

There was no apparent trend for compositions of copolymer. The copolymers irradiated at different wavelengths have similar compositions (average m_d = 0.406-0.416). It indicated that the same propagation process was employed for both wavelengths. For a typical 1:2 copolymer and a 1:1 copolymer, m_d is 0.33 and 0.50 respectively. The compositions of both copolymers fell in the range from 0.351 to 0.486 within a wide range of feed compositions. Together with the spectroscopic data this is the basis of assuming a copolymer containing both the 1:1 and 1:2 copolymer structures XXIV. Note that is is not necessarily a block copolymer in the sense of 1:1 and 1:2 monomer combinations. The 1:1 repeating unit has been found in the copolymerization of p-dioxene-MAH,[77] DVE-DMTHNQ and DVE-THNQ systems,[43] in which the homopolymerization of a 1:1 CTC was considered.

XXV
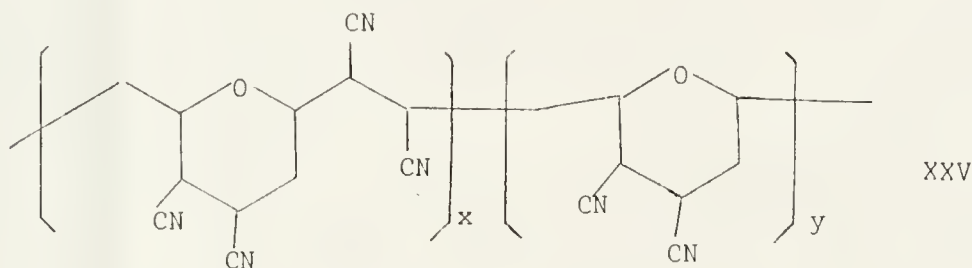
When the reaction time of copolymerization was long enough so that the reaction was almost completed, it was observed that the yield at 236 nm for large excess of DVE in feed composition was more than the corresponding theoretical maximum of conversion of a perfect 1:2 copolymer but less than or close to the 1:1 copolymer (Table X). At 300 nm the yield was less than the theoretical 1:2 copolymer.

The excess yield at 236 nm can be explained by the involvement of either the homopolymerized DVE or the 1:1 copolymer structure in the 1:2 overall copolymer structure. When FN is about used up at the end of the

reaction, homopolymerization of DVE has a chance to compete with the copolymerization. The fraction of DVE in copolymer (m_d) supports the involvement of homopolymerization of DVE. What is important is that the close value of m_d at both 300 nm and 236 nm (m_d = 0.56±0.03) indicating that the involvement of homopolymerization is in the propagation process instead of the initiation process, in other words, in the early stage of the copolymerization, the homopolymerization is not involved.

Table X

The Limiting Yield of Copolymerization with
Excess DVE in Feed Composition

Wavelength (nm)	Feed Composition FN%	Yield (mg)	Theoretical Yield (mg)[b]		m_d [a, c]
			1:2 Copolymer	1:1 Copolymer	
300	2	24.8	32.5	---	--
	5	40.1	49.7	---	--
	10	115.7	135.1	---	0.54
236	1	25.7	24.8	32.5	0.59
	2	45.1	32.5	42.5	--
	5	78.9	57.3	75.0	0.52
	10	161.0	143.7	188.2	0.57

[a] The fraction of DVE in copolymer calculated from nitrogen and carbon content.
[b] Based on the reacted amount of FN.
[c] Average = 0.56.

The different initiating wavelength would finally form the same intermediate or intermediates which initiates the same propagating radicals. The structure of this copolymer can be further confirmed by ^{13}C nmr spectroscopy.

The ^{13}C nmr spectra.   The ^{13}C nmr spectrum of the copolymer is
shown in Fig. 14.   The four peaks at δ 118.5, 117.9, 116.6, and 116.1
ppm from TMS in the CN region supports the six-membered ring structure
where two of them correspond to the two unsymmetrical CN's on the ring
and the other two correspond to the CN's on the skeleton.

It was pointed out in Chapter II that the small difference between
the two carbonyl carbons would only cause a broadening of the peak
instead of splitting it.   This assumption can be applied here that the
doublet of each CN peak does not indicate two non-equivalent CN's in
the ring or on the backbone.   The chemical shift difference (0.5-0.6 ppm)
between each peak in the doublet is close to the difference of the carbonyl
peaks of dl-meso mixture of 2,3-dimethyl succinic acid (0.9 ppm).   We
can assign the doublet as the consequence of the mixture of cis- and trans-
dicyano substitutions on each fumaronitrile unit. These assignments will
lead to a reasonable conclusion that in backbone, cis- and trans-disubstitu-
tions are more or less equally populated, by considering the equal
intensities of the doublets as shown on the peaks at δ 117.9 and 118.5 ppm.
The CN's at δ 116.6 and 116.1 ppm indicated the different populations of
cis- and trans-disubstitutions, which are possible during the ring formation.

It is difficult to assign the chemical chifts of the CN groups
without comparing with model compounds, but at least a copolymer with
the 1:1 and 1:2 copolymer composition is consistent with the spectra.

The two C-O-C peaks in the C-O-C region indicated the existence of
two different C-O-C linkages in the copolymer.   Comparing the ^{13}C nmr
spectra of homopolymers of DVE with the copolymers enabled us to clarify
the exclusion of homopolymer structure in the copolymer.[78]   (Table XI)
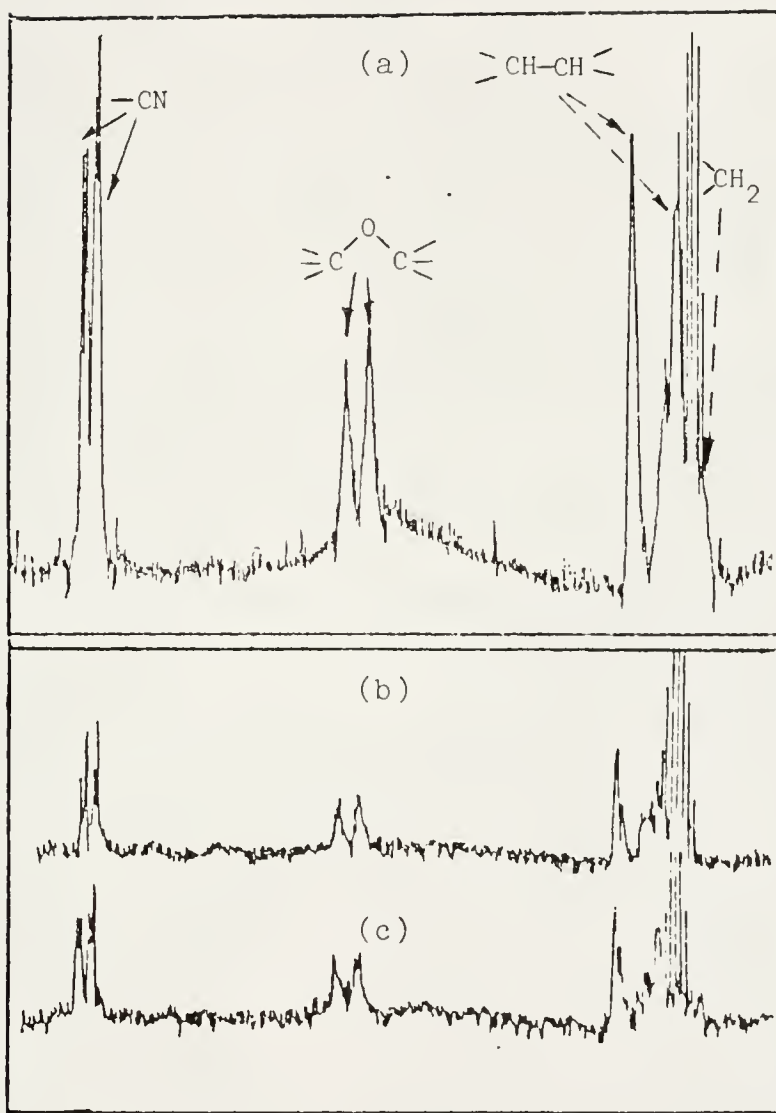
Fig. 14 ^{13}C nuclear magnetic resonance spectra of the copolymer initiated (a) at 236 nm, (b) by AIBN, (c) at 300 nm.

Table XI

Comparison of ^{13}C nmr Spectra Between Homopolymer of DVE and
the Copolymer of DVE and FN

Material	Chemical Shift (ppm from TMS) of C*'s	No. of CN Substitutions on C*'s	Calculated total shift (ppm)
Homopolymer			
XXVIII	82.3, 83.4, 151.1		
XXIX	84.2		
XXX	77.8		
Copolymer			
XXVI	79.6	α, 0; β, 1; γ, 2	+11
XXVII	76.7	α, 0; β, 1; γ, 1	+10

*The special carbon in consideration.

XXVIII   XXIX   XXX

XXVI

XXVII
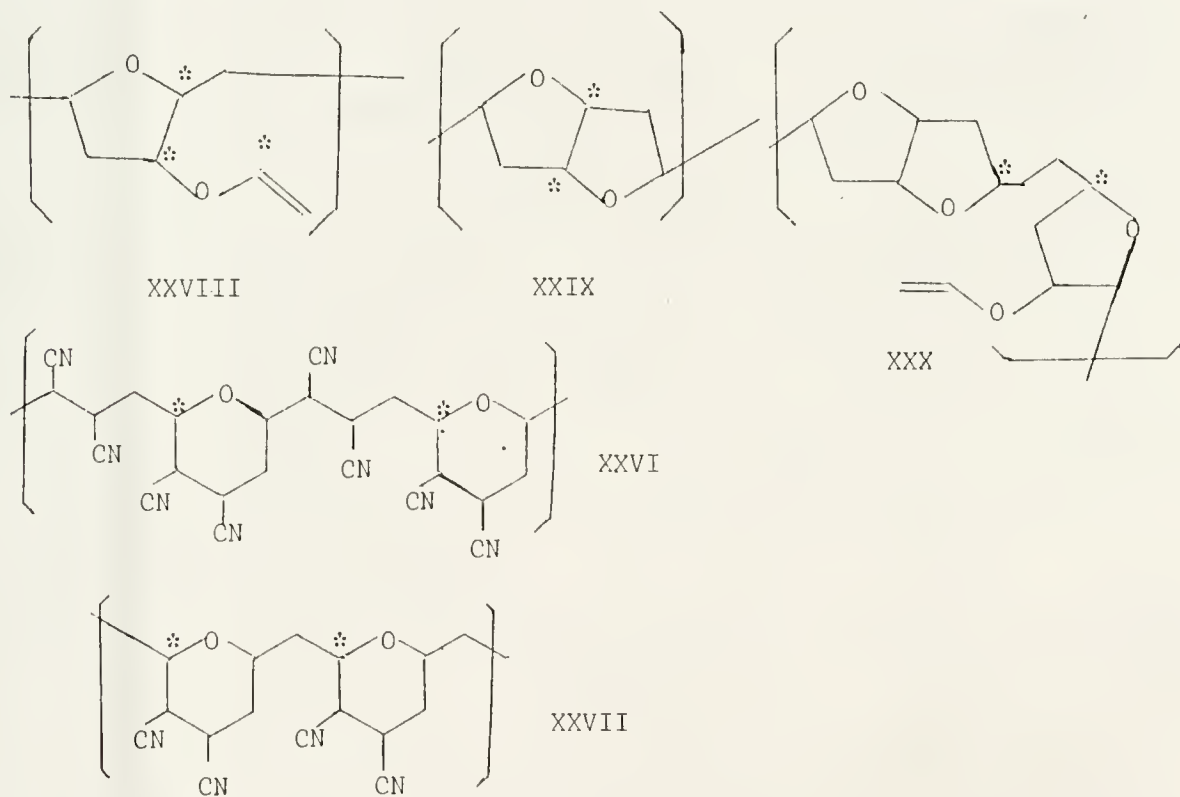
Comparing the C^*'s in trimethyleneglycol (two oxygens are three carbons apart) with pentamethyleneglycol (two oxygens are five carbons apart), there is a 2.9 ppm difference in chemical shift due to the distance of the two oxygens.[79] The 2.9 ppm difference of the two C-O-C absorption in the copolymer can then be explained by comparison between the C^*'s in structure XXVII and then XXVI.

HO∿∿∿OH $*$

59.2 ppm

HO∿∿∿∿OH $*$
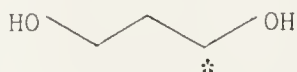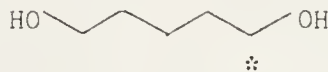
62.1 ppm

In conclusion, at low conversion, the copolymer contained a mixture of structures XXVI and XXVII, a small amount of residual unsaturation and probably some homopolymer structure which can be neglected for kinetic consideration. The average $m_d = 0.41$ corresponding to a 56% of structure XXVII. This ratio of structure XXVI to structure XXVII was reflected by the almost equal intensity of the two C-O-C absorption in ^{13}C nmr spectra.

To distinguish between pure five- and six-membered ring structures is very difficult because of the lack of information. As discussed in Chapter II, it is unlikely to have a mixture of both six- and five-membered rings structures in the copolymer because of the simplicity of the spectrum. Furthermore, a favorable conformation of the complex and the orientation of the cyclization makes the six-membered ring structure more possible.

Quantum Yield Study

Quantum yields for formation of copolymer were measured in aceto-
nitrile and at different wavelengths. The intensities are different at
different wavelengths for monochromatic light source. It will be pos-
sible to compare the quantum yields at different wavelengths by knowing
the dependence of intensity on quantum yield.

The data obtained for 0.6 m/l FN and 0.6 m/l DVE in acetonitrile
at 300 nm showed small dependence on light intensities. The intensity
was altered by using different slits.

The quantum yields were not exactly independent of the intensity
for nonequal molar solutions with 0.47 m/l of FN and 0.71 m/l of DVE
in acetonitrile at 300 nm. The intensities were altered either by
the different slits or with a copper screen in front of the sample tube
in this case. Also, the quantum yields were changed with different
intensities at 236 nm, with 0.6 m/l of DVE and 0.6 m/l of FN. The data
of the light intensity dependence on qauntum yeild and rate are listed
in Table XII.

The linear dependence of intensity on quantum yield are shown in
Table XIII. The linear correlation coefficients were close to one
indicating that the equations can be used for comparing the quantum
yields at the same intensity for different wavelengths. The results are
shown in Table XIV. Apparently the quantum yield at 236 nm is larger
than at 300 nm.

Ferree and Butler observed that the quantum yield was constant or
declined slightly as the wavelengths decreased, until part of the divinyl
ether band is excited at 236 nm, at which point the quantum yield in-
creased drastically.[58] This fact suggests that only excitation in either

Table XII

The Light Intensity Dependence on Quantum Yield and Rate in
Acetonitrile at Room Temperature

Concentration (m/l)		Wavelength (nm)	Light Intensity photons/sec	Quantum Yield	Conversion %	Rate mg/min
DVE	FN					
0.6	0.6	300± 3.2	3.48×10^{-15}	0.062	2	0.098
		300± 9.6	2.37×10^{16}	0.049	4	0.54
		300±12.8	3.29×10^{16}	0.059	11	0.88
		300±16.0	5.61×10^{16}	0.052	5	1.31
0.47	0.71	300±12.8	4.41×10^{16}	0.038	1	0.761
		300± 6.4	1.41×10^{16}	0.044	2	0.285
		300± 6.4	5.7×10^{15}	0.054	2	0.140
		300± 6.4	0.77×10^{15}	0.079	2	0.026
0.6	0.6	236±22.4	115×10^{14}	0.048	3	0.25
		236±16.0	73	0.051	2	0.17
		236±16.0[a]	59	0.056	2	0.15
		236± 9.6	25.5	0.068	2	0.079
		236± 9.6[a]	7.4	0.095	2	0.032
		236± 6.4	7.8	0.102	2	0.036
		236± 3.2	3.4	0.126	---	0.019

[a] With a copper screen in front of the sample tube.
[b] With a copper screen fold twice in front of the sample tube.

Table XIII

The Linear Relations of Intensity (I) to the Quantum Yields (Φ) and Rates

Wavelength (nm)	Concentration (m/l)		Linear Dependence Equations[a]	Correlation Coefficient
	FN	DVE		
300	0.6	0.6	$\log(\Phi \times 10^2) = -0.06 \log(I \times 10^{-15}) - 1.8$	
			$\log(\text{rate} \times 10^2) = -0.457 + 0.94 \log(I \times 10^{-14})$	0.99
300	0.47	0.71	$\log(\Phi \times 10^2) = -0.18 \log(I \times 10^{-14}) + 1.5$	0.98
			$\log(\text{rate} \times 10^2) = -0.293 + 0.821 \log(I \times 10^{-14})$	1.00
236	0.6	0.6	$\log(\Phi \times 10^2) = -0.271 \log(I \times 10^{-14}) + 1.23$	0.99
			$\log(\text{rate} \times 10^2) = -0.104 + 0.72 \log(I \times 10^{-14})$	0.99

[a]Rate is in mg/min. I is in photons/sec.

the charge transfer complex absorption band or the divinyl ether
absorption band leads to initiation of copolymerization.

Table XIV

Comparison of Quantum Yield and Rate at 236 nm and 300 nm

Compound	Concentration	Wavelength (nm)	Intensity Photons/sec	Quantum Yield	Rate mg/min.
FN	0.47 m/l	236	8.86×10^{14}	0.118	0.479
DVE	0.71 m/l	300	8.86×10^{14}	0.076[a]	0.304[a]

[a]Calculated from equations in Table XIII.

It has been suggested that an exciplex was responsible for the
copolymerization while no ground state charge transfer complex was
observed,[76] such as the photocopolymerization of vinylcarbazol and
acrylonitrile. Since at 236 nm the only effective photoabsorbing
species was DVE, the initiation process must proceed via the excited
state of DVE. Although there was no evidence of exciplex of DVE and FN,
no significant homopolymerization was obtained with DVE alone, this
fact indicating that the excited DVE initiated copolymerization possibly
through the interaction with the ground state of FN.

$$DVE \quad \xrightarrow{\text{236 nm}} \quad (DVE)*$$

$$(DVE)* + FN \longrightarrow (DVE* \to FN)$$
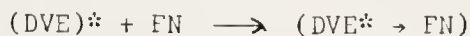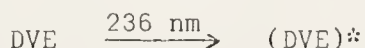
exciplex

At 300 nm the photoabsorbing species was complex, therefore the initiation process proceeded _via_ the excited state of the complex.

$$\text{DVE} + \text{FN} \;\rightleftharpoons\; (\text{DVE} - \text{FN}) \xrightarrow[300\ nm]{} (\text{DVE} \rightarrow \text{FN})^*$$
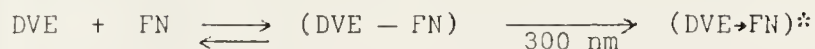
At both wavelengths, the excited species dissociated into initiating radicals. Although the initiating radicals have not been identified they could be a paired cationic radical and anionic radical.

$$(\text{DVE} \rightarrow \text{FM})^* \xrightarrow{\;k_d\;} 2\text{R}\cdot$$

$$(\text{DVE}^* \rightarrow \text{FN}) \xrightarrow{\;k'_d\;} 2\text{R}\cdot$$

The ionic radicals initiated the copolymerization through free radical processes because both air and a small amount of diphenylpicryl-hydrazyl free radical (DPPH) retarded the reaction.
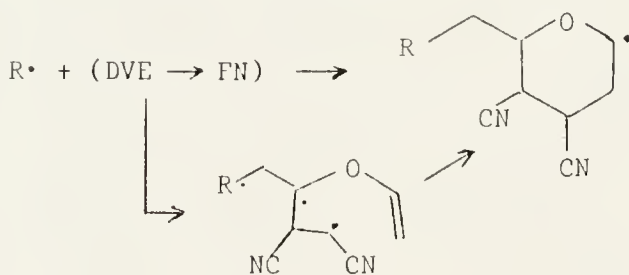
A small amount of FN (1%) did not initiate the homopolymerization of large excess DVE (99%) to a significant extent. This indicated that the divinyl ether radical formation can be excluded at least in the early stages of the copolymerization.

The initiation through free fumaronitrile cannot be excluded but probably is not able to compete with the low energy pathway of the complex initiation process.

At 300 nm the light was totally absorbed by the complex for the solution of 1.2 m/l and of FN and 1.2 m/l of DVE.

$$FN + DVE \rightleftharpoons (DVE \rightarrow FN) \xrightarrow[\,I_c\phi_c\,]{300\ nm} (DVE \rightarrow FN)^* \xrightarrow{k_d} 2R\cdot$$

$(DVE \rightarrow FN)^*$ is the excited complex.

$$(DVE \rightarrow FN)^* \begin{array}{l} \xrightarrow{\;(DVE)\;} \\[6pt] \xrightarrow{\;(FN)\;} \\[6pt] \xrightarrow{\;(DVE \rightarrow FN)\;} \end{array} \quad \text{Ground state molecules}$$
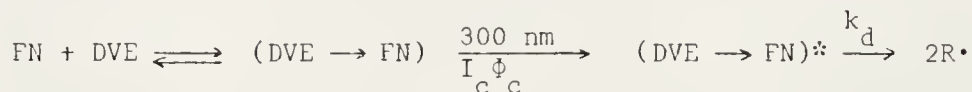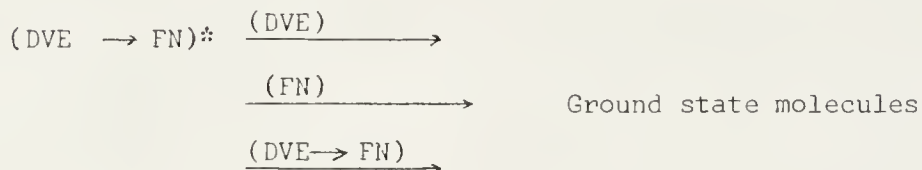
Scheme II

I_c = The light intensity absorbed by the complex.

= I_{abs} (light intensity absorbed by actinometer).

ϕ_c = The quantum yield with only radiation deactivation considered.

The excited complex may be deactivated by collision processes. As discussed before the exact structure of the excited state is not known, but it may still be very polar and very likely to be deactivated by the polar monomers and the ground state complex. The radiationless deactivation process may be proposed as in Scheme II.

The rate of formation of the primary radicals ($R\cdot$) can be derived by applying the steady state assumption and assuming that the radiationless rates of the deactivation of excited complex is proportional to the total concentration of monomers, (T).

$$\left(\frac{-d(DVE \rightarrow FN)^*}{dt} \right)_{rl} = k_{rl}(T)(DVE \rightarrow TN)^*$$

Therefore,

$$\frac{d(DVE \rightarrow FN)^*}{dt} = I_c\Phi_c - (DVE \rightarrow FN)^*(k_d + k_{rl}(T)) = 0$$

From Scheme II

$$R_i = k_d(DVE \rightarrow FN)^* = (k_d I_c \Phi_c)/(k_d + K_{rl}(T))$$

At 236 nm the complex absorbed insignificantly but DVE absorbed part of the light, $I_d = I_{abs}\epsilon_d(DVE)$, and is responsible for the initiation through the following equation.

$$DVE \xrightarrow[I_d\Phi_d]{236\ nm} DVE^* \xrightarrow[k_{df}]{FN} (DVE^* \rightarrow FN) \xrightarrow{k'_d} 2R\cdot$$

$$\xrightarrow[\text{radiationless deactivation}]{k'_{rl}}$$
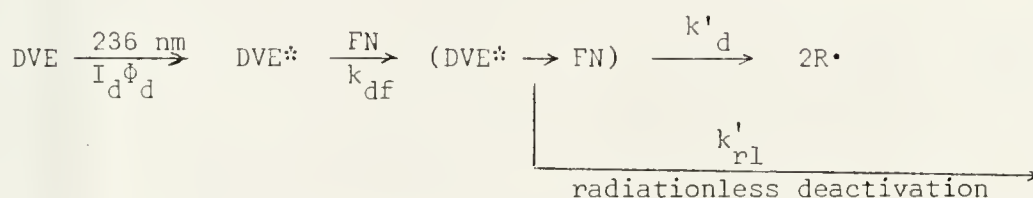
Φ_d is the quantum yield with only radiation deactivation considered.

In the same way as proposed at 300 nm, the rate of formation of the primary radicals (R·) can be derived by assuming the rate of the deactivation of exciplex, $\left(- \dfrac{d(DVE^* \rightarrow FN)}{dt}\right)_{rl'}$ is proportional to the total concentration of monomers (T).

$$\frac{d(DVE^* \rightarrow FN)}{dt} = k_{df}(DVE^*)(FN)-(DVE^* \rightarrow FN)(k'_d + k'_{rl}(T)) = 0$$

$$R_i = k'_d(DVE^* \rightarrow FN) = \frac{k'_d I_{abs}\Phi_d\epsilon_d(DVE)}{k'_d + k'_{rl}(T)}$$

Dependence of Feed Composition on Rates

It was of considerable interest to measure the rate of copolymeriza-
tion obtained for different feed compositions. As explained later, the
study of the rate as a function of the feed composition when the total
monomer concentration is kept constant should give information on the
role of the charge transfer complex in the mechanism of copolymeriza-
tion.

The effect of the variation of the concentration of the reactants
on the rate of a photochemical reaction is difficult to determine
unless the rates are corrected to a constant absorbed light intensity
from known variation of rate with the absorbed light intensity.

The rate of copolymerization was measured in acetonitrile. The
samples were prepared as indicated in the experimental section. The
solutions were irradiated at room temperature for a measured period
of time and the reaction was stopped by immediately opening and roto-
vapping to dryness. Methanol was added, and the insoluble polymer was
filtered and washed with methanol, and dried in an oven at 50°C at least
for 4 hours. The actinometer solution was irradiated in the same tube
right after the reaction. The rate was obtained by measuring the
weight of the polymer after drying. The dependence of the light
intensity on rate is reported in Table XII. The linear relation is
shown in Table XIII.

Rates of products formed in secondary reactions (including the
polymerization) usually show some other than first order dependence
on intensity. In general, bimolecular termination by a reaction
involving active chain carrying species results in rates proportional
to the square-root of intensity. Termination which occurs from a first

order reaction leads to a rate which is dependent on the first power of intensity. It was observed that the rates were dependent on an order between 0.72 - 1 of intensity. It was close to first order for the equal molar solution at 300 nm. Possibly both the bimolecular and unimolecular termination are operating in photocopolymerization. The first order termination is more possible because the propagating radical may be terminated by chain transfering to solvent and the polar monomers. The dependence of feed composition on corrected rate was listed in Table XV and XVI and Fig. 15 and 16.

The rates were compared at $I = 1.52 \times 10^{16}$ photons/sec and 6.4×10^{14} photons/sec for irradiation at 300 nm and 236 nm respectively. It was observed that at 300 nm, the maximum rate was at $f_d = 0.5$ (equal molar solution), but at $f_d > 0.5$ at 236 nm for both total concentration [(T) = 2.40 m/l and 0.60 m/l]. The composition of copolymers were in the same range (m_d = 0.35-0.48), and not much different from each other for both wavelengths. Interestingly, at 236 nm, the rate maximum fell on f_d = 0.66 and 0.80 for higher total concentration, (T) = 2.00 m/l, but on f_d = 0.55-0.80 for lower total concentration, (T) = 0.60 m/l. The ir and nmr spectra were almost identical. These facts indicated that the same propagation process was employed. The different positions of rate maxima were then due to the different initiation porcesses.

Mechanisms

The kinetical derivation of the overall rate of copolymerization can be done by assuming the simplest propagation as follows.

$$(Eq. 22)$$

$$(Eq. 23)$$

Table XV

The Rate of Copolymerization of DVE-FN System in Acetonitrile
at 300 nm, at I = 1.52 x 10^{16} Photons/Sec.

Total Concentration (m/l)	f_d	Rate[a] (mg/min)	Total Concentration (m/l)	f_d	Rate[a] (mg/min)
0.60	1.00	nil	1.20	0.80	0.179
0.60	0.90	0.051	1.20	0.60	0.313
0.60	0.82	0.117	1.20	0.50	0.376
0.60	0.80	0.098	1.20		
0.60	0.70	0.131	2.40	0.98	0.087
0.60	0.67	0.154	2.40	0.70	0.475
0.60	0.60	0.150[c]	2.40	0.60	0.604
0.60	0.55	0.154	2.40	0.50	0.749
0.60	0.52	0.185	2.40	0.33	0.580
0.60	0.50	0.198	2.40		
0.60	0.45	0.161	2.40		
0.60	0.40	0.190	2.40		
0.60	0.40[b]	0.053	2.40		
0.60	0.30	0.167	2.40		
0.60	0.20	0.147	2.40		
0.60	0.00	---	2.40		

[a]The rates were corrected to I = 1.52 x 10^{16} photons/sec with equation
log rate$_{cal}$/rate$_{exp}$ = log 1.52/I$_{exp}$ x 10^{-16}.

[b]Sample was open to air.

[c]Average values.
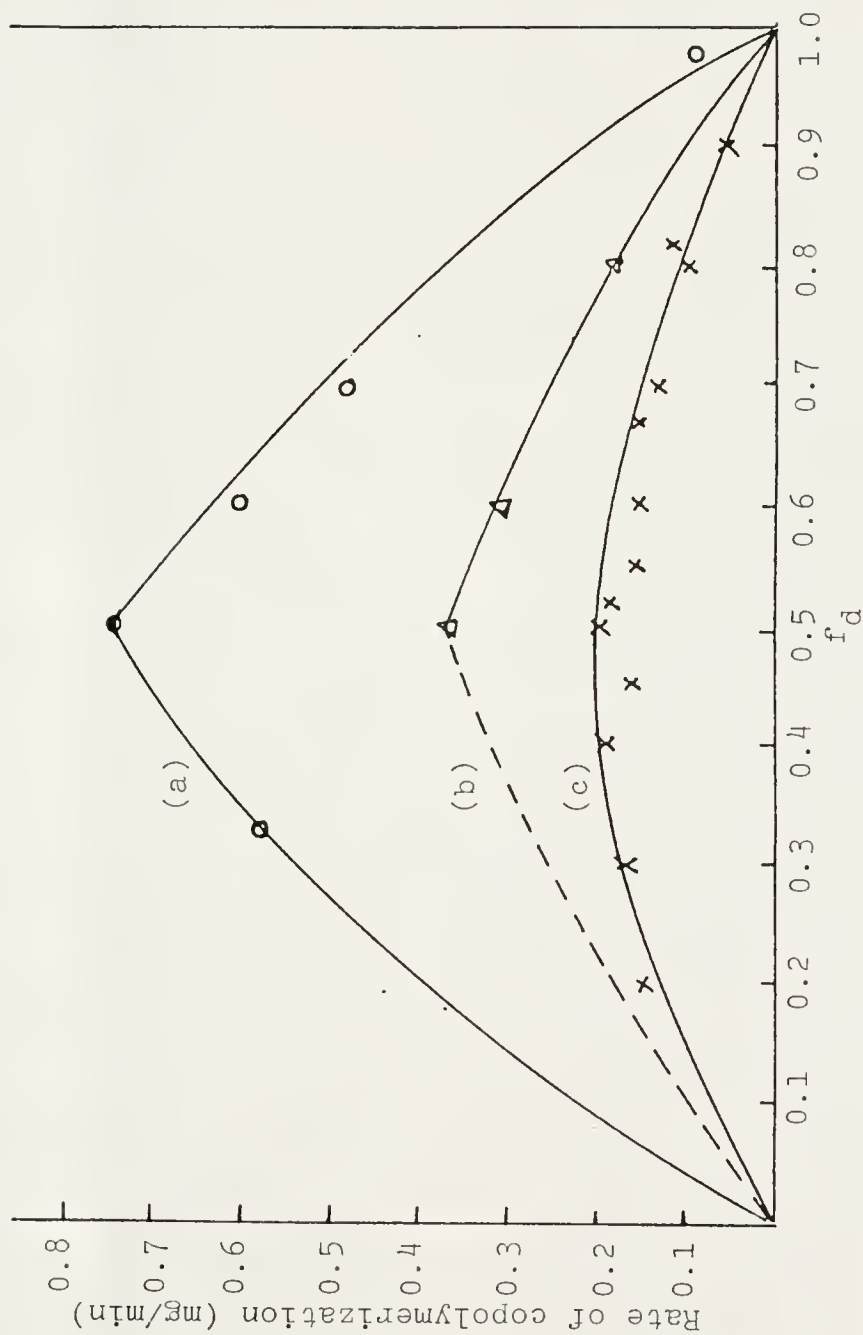
Fig. 15 The dependence of feed composition on rate at 300 nm ($I = 1.52$ x 10^{16} photons/sec) for total concentration (a) 2.40 m/1, (b) 1.20 m/1, (c) 0.60 m/1.
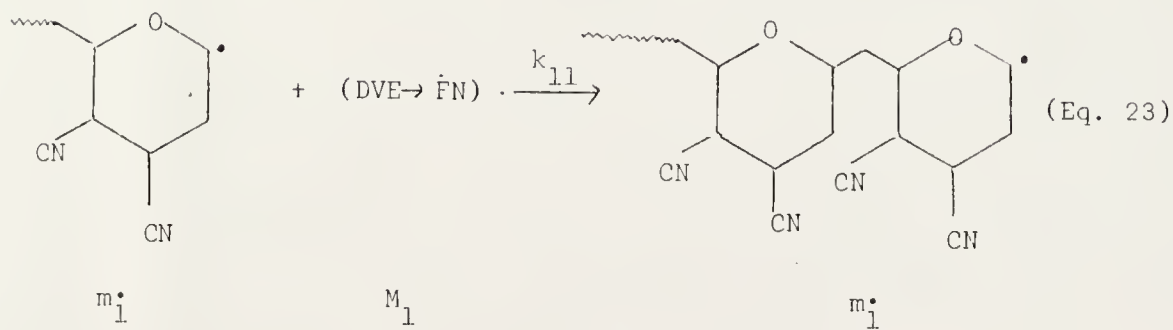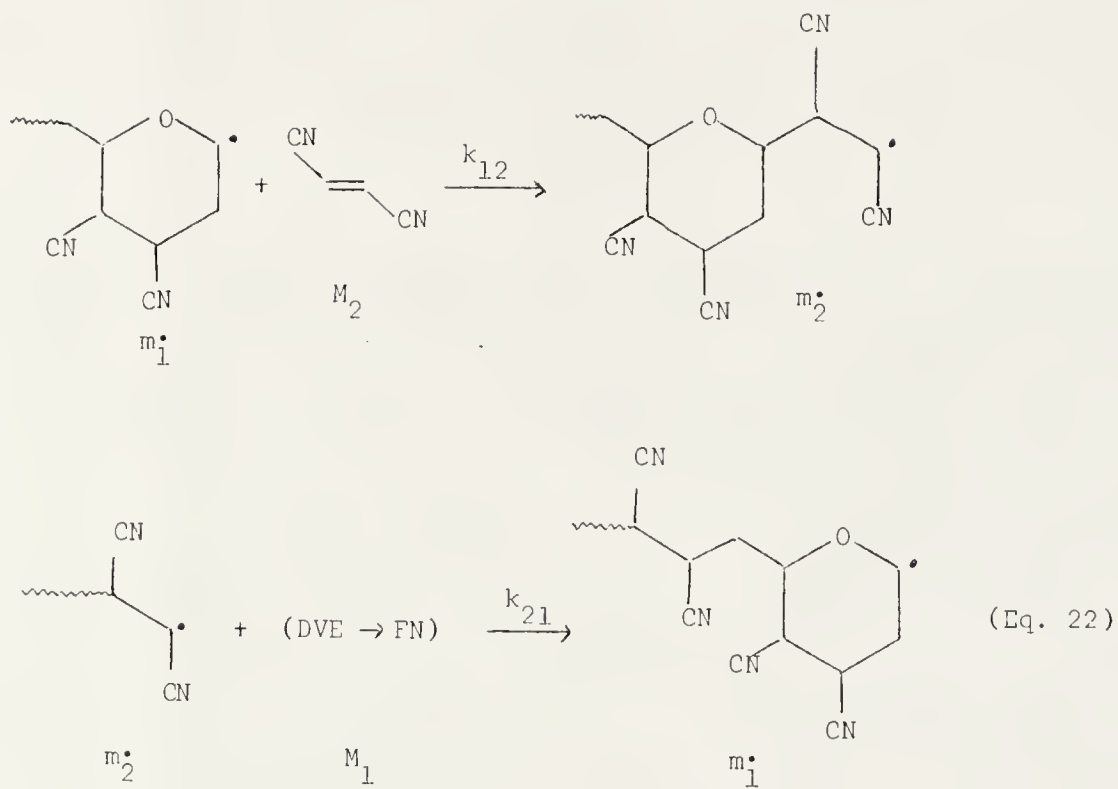
Table XVI

The Rate of Copolymerization of DVE-FN System in Acetonitrile
at 236 nm, at $I = 6.4 \times 10^{14}$ Photons/Sec.

Total Concentration (m/l)	f_d	Rate[a] (mg/min)	Total Concentration (m/l)	f_d	Rate[a] (mg/min)
0.60	1.00	nil	2.00	0.90	0.0413
0.60	0.90	0.0217[c]	2.00	0.80	0.0692
0.60	0.80	0.0274[c]	2.00	0.80[b]	0.0267
0.60	0.70	0.0231[c]	2.00	0.66	0.0686
0.60	0.60	0.0229[c]	2.00	0.50	0.0644
0.60	0.55	0.0303	2.00	0.40	0.0448
0.60	0.50	0.0246[c]	2.00		
0.60	0.48	0.0235	2.00		
0.60	0.45	0.0170[c]	2.00		
0.60	0.41	0.0197	2.00		
0.60	0.40	0.0179	2.00		
0.60	0.31	0.0209	2.00		
0.60	0.00	---	2.00		

[a] The rates were corrected to $I = 6.4 \times 10^{14}$ photons/sec with the equation
$\log \text{rate}_{cal}/\text{rate}_{exp} = 0.72 \log 6.4/I_{exp} \times 10^{-14}$.
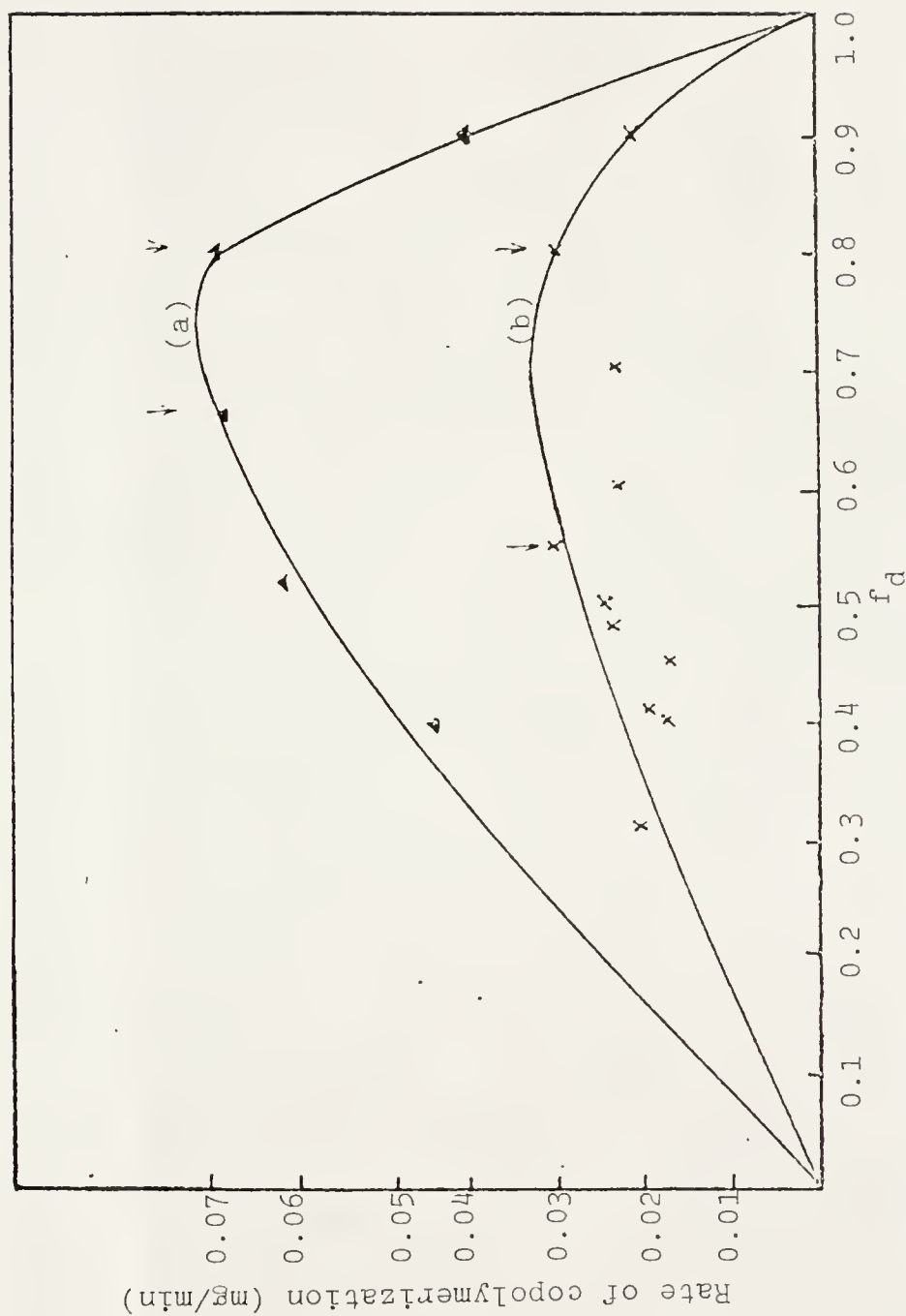
[b] Sample was open to air.

[c] Average value.

Fig. 16 The dependence of feed composition on rate at 236 nm (I = 6.4 x 10^14 photons/sec) for total concentration (a) 2.0 m/l, (b) 0.6 m/l.

In this copolymerization, the cyclized DVE radical (XXXI)
attacked complex and monomers to produce polymers with 1:1 and 1:2
compositions, respectively. The 1:1 composition cannot be explained
by the polarity of the radical and complex, because the negatively
polarized radical (XXXI) would attack the positively polarized carbon
carbon double bond of an acceptor monomer since polymerization of DVE
under the same condition is negligible. The propagation of the copoly-
merization can be interpreted as a competition between the acceptor
monomer FN and the CTC toward the cyclized DVE radical (XXXI).

Although the cyclization of the DVE radical (XXXI) could react
preferably with the acceptor such as MAH because the reaction of a
radical and a monomer of opposite polarities would stabilize the
transition state,[80] the FN may not be so preferable because of the
less polarization then MAH. Thus, the reactivities of FN and the complex
are compatible. As a result, a competition between FN and CTC control
the structure of the copolymer of DVE-FN system. On the other hand,
the complexation of the HOMO of DVE and LUMO of FN would increase the
energy of HOMO of DVE[71] and make the CTC more reactive toward the
destabilized cyclized radical (XXXI) than the uncomplexed DVE.

In equations 22 and 23, the cyclization may proceed by both
concerted and stepwise processes. A fast cyclization has been observed
for this cyclocopolymerization, which indicated a concerted mechanism.
But some results showed the stepwise mechanism, especially for the
fact that both cis and trans disubstituted ring units were obtained in
the analysis of spectra. A stepwise cyclization cannot be ruled out.
However, by assuming a fast stepwise cyclization (probably just a little
slower than the cis-trans rotation around the disubstituted single bond)

of radical XXXII, the same result will be concluded as with the

concerted process as far as rate is concerned.
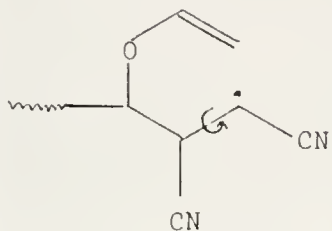
XXXII

By assuming only the cross-termination

$$m_1\cdot + m_2\cdot \xrightarrow{k_{t12}} \text{dead polymer}$$
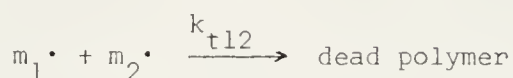
and the steady state:

$$k_{12}(m_1\cdot)(M_2) = k_{21}(m_2\cdot)(M_1)$$

$$R_i = R_t = 2k_{t12}(m_1\cdot)(m_2\cdot) = 2k_{t12}\frac{k_{12}(M_2)}{k_{21}(M_1)}(m_1\cdot)^2$$

Then, by assuming $(DVE \rightarrow FN) \simeq K_c(FN)(DVE)$

$$\text{Rate} = (\frac{R_i k_{21}}{2k_{12}k_{t12}})^{1/2}(DVE)^{1/2}(FN)K_c^{1/2}[2k_{12} + k_{11}K_c(DVE)]$$

By definition $(FN) = (1 - f_d)(T)$, $(DVE) = f_d(T)$

where $(T) = $ total concentration $= (FN)+(DVE)$, $f_d = (DVE)/(T)$

The rate maximum is a function of (T) and will be at $f_d = 0.5$ by keeping

(T) constant, only when

$$(DVE) = \frac{2k_{12}}{k_{11}K_c}$$

This was not the case for copolymerization irradiated at 300 nm where the maximum rate was at $f_d = 0.5$ for $(DVE) = 1.2$ m/l at $(T) = 2.40$ m.l and $(DVE) = 0.3$ m/l at $(T) = 0.60$ m/l.

By assuming the noncoupling termination as suggested by the relationship between rate and intensity,

$$R_i = R_t = k_t(m_1^. + m_2^.) = k_t(\frac{k_{21}M_1}{k_{12}M_2} + 1)(m_2^.)$$

$$Rate = 2k_{12}M_2(m_1^.) + k_{11}M_1(m_1^.) = \frac{k_{21}K_cR_i}{k_t}(FN)(DVE)\frac{[2k_{12} + k_{11}K_c(DVE)]}{[k_{12} + k_{21}K_i(DVE)]}$$

As discussed before, $K_c = 0.10$ l/mole, therefore, for a solution with 1.2 m/l of DVE and 1.2 m/l of FN in acetonitrile,

$$(DVE \longrightarrow FN) \simeq K_c(DVE)(FN) = 0.144 \text{ m/l}.$$

The concentration of complex existing in the solution is of the order of 10% of the monomers. The reactivity of the complex must be very large compared to the monomers in order to compete with the free monomer addition.

By assuming $k_{21}, k_{11} >> k_{12}$

$$k_{11}K_c(DVE) >> 2k_{12}$$

$$k_{21}K_c(DVE) >> k_{12}$$

Then

$$Rate = \frac{k_{11}K_cR_i}{k_t}(FN)(DVE)$$

If R_i is independent of monomer concentration, rate will reach maximum at f_d = 0.5 by keeping (T) constant.

This was the case for copolymerization of DVE and FN in aceto-nitrile at 300 nm with (T) = 2.40 m/l, 0.60 m/l.

As discussed before, R_i is a function of concentration and should be considered in the rate derivation. At 300 nm,

$$R_i = [k_d I_{abs} \phi_c]/[k_d + k_{rl}(T)] \quad \text{where } I_{abs} = I_c \text{ at 300 nm.}$$

$$\text{Rate} = \frac{k_{11} K_c k_d I_{abs}}{k_t} [\phi_c (FN)(DVE)]/[k_d + k_{rl}(T)]$$

When (T) is kept constant, the rate maximum will be at f_d = 0.5.

If f_d is kept constant instead, by variation of the total concentration, the rate will be linear to (T).

$$(DVE) = f_d(T), \quad (FN) = (1-f_d)(T), \quad f_d = \frac{(DVE)}{(T)}$$

$$\text{Rate } \alpha \quad \frac{(FN)(DVE)}{k_d + k_{rl}(T)} = \frac{(1-f_d)f_d(T)^2}{k_d + k_{rl}(T)}$$

The deactivation process is usually quite large compared to the dissociation.

$$k_{rl}(T) >> k_d, \quad R_i = k_d I_{abs} \phi_c / k_{rl}(T) \qquad \text{(Eq. 24)}$$

then,

$$\text{Rate } \alpha \ (T)^2 / k_{rl}(T) \ \alpha \ (T).$$

This fact was confirmed by Table XVII and Fig. 17, where the rate is proportional to (T), (slope = 1.0) at f_d = 0.6 and 0.5.

Table XVII

The Dependence of Total Concentration on Rate

Wavelength	f_d	(T) m/l	Rate[a](mg/min)	Slope[b]	C[b]
300 nm	0.50	0.60	0.198	0.96	0.998
300 nm	0.50	1.20	0.376		
300 nm	0.50	2.40	0.749		
300 nm	0.60	0.60	0.150[c]	1.00	0.994
300 nm	0.60	1.20	0.313		
300 nm	0.60	2.4	0.604		
236 nm	0.60	0.60	0.0246[d]	0.77	0.839
236 nm	0.60	1.20	0.0300[e, d]		
236 nm	0.60	2.00	0.0644[d]		
236 nm	0.80	0.60	0.0274[d]	0.77	1.00
236 nm	0.80	2.00	0.0692[d]		

[a]Rates were corrected to $I = 1.52 \times 10^{16}$ photons/sec.

[b]The slope of the equation: log rate = a + b log (T)
 C is the correlation coefficient.

[c]Average value.

[d]Rates were corrected to $I = 6.4 \times 10^{14}$ photons/sec.
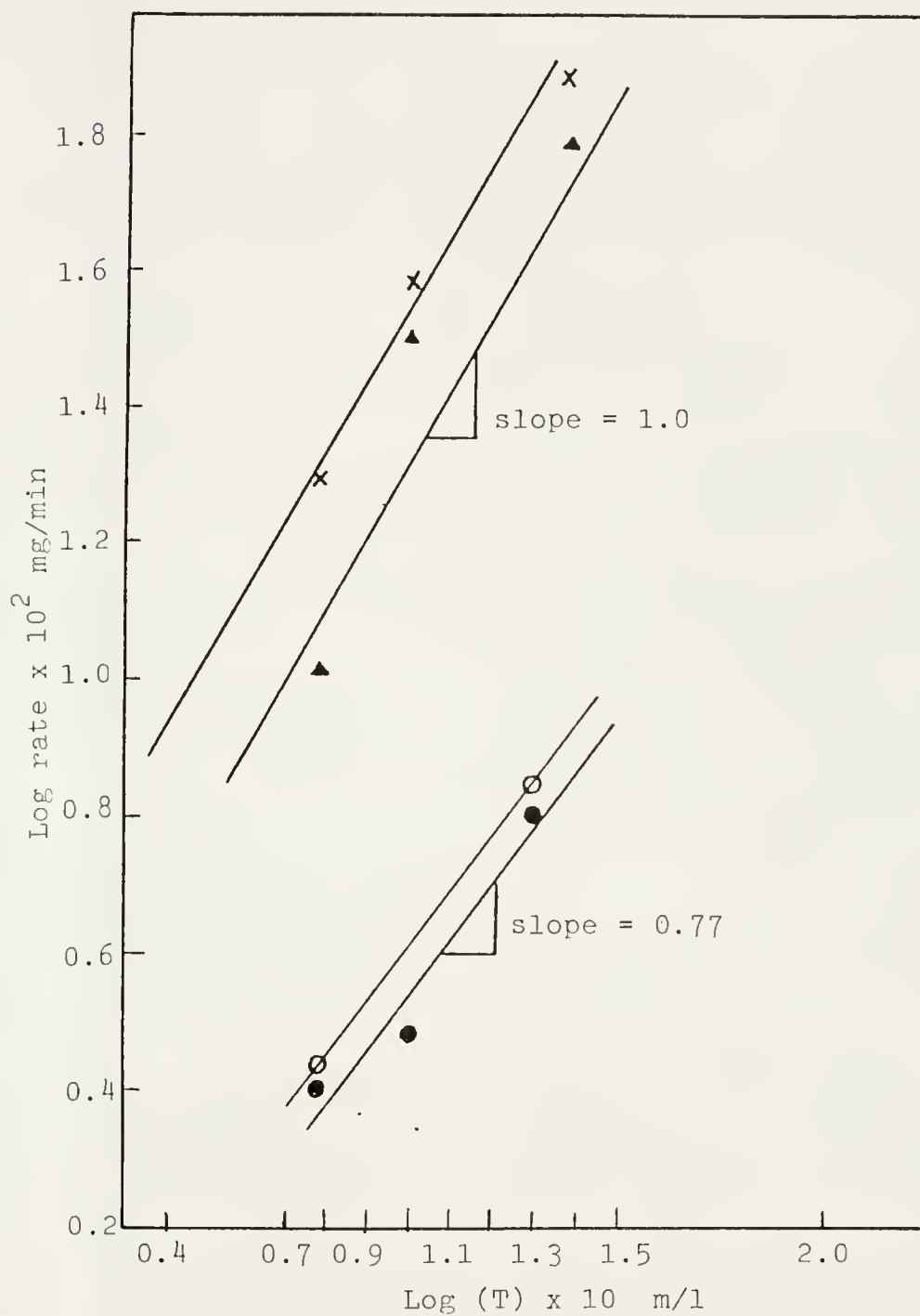
[e]Calculated from equation in Table XV.

Fig. 17 The dependence of total concentration on rate
(x) at 300 nm, f_d = 0.5, (▲) at 300 nm, f_d = 0.6
(o) at 236 nm, f_d^d = 0.5, (●) at 236 nm, f_d^d = 0.8

At 236 nm,

$$R_i = \frac{k_d' I_{abs} \Phi_d \epsilon_d (DVE)}{k_d' + k_{rl}'(T)} \simeq \frac{k_d' I_{abs} \Phi_d \epsilon_d (DVE)}{k_{rl}'(T)} \quad \text{where } (k_{rl}'(T) >> k_d')$$

$$\text{Rate} = \frac{k_d' k_{11} K_c I_{abs}}{k_t} \; [\Phi_d \epsilon_d (DVE)^2 (FN)]/[k_{rl}'(T)]$$

When (T) is kept constant,

Rate α $(DVE)^2(FN)$

Rate will be maximum at $(FN)/(DVE) = 1/2$

i.e. $f_d = 2/3$, the rate maximum is at DVE rich region.

This is similar to the case observed for copolymerization of DVE and FN with (T) = 2.00 m/l where the rate maximum was in the DVE rich region, $f_{d, max} > 2/3$, probably due to the fact that both the excited DVE and the exciplex (DVE* → FN) are more or less preferred to be deactivated by FN through polar coupling.

(DVE* → FN)
↑
FN   ground state molecules
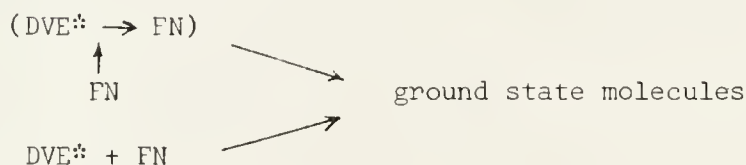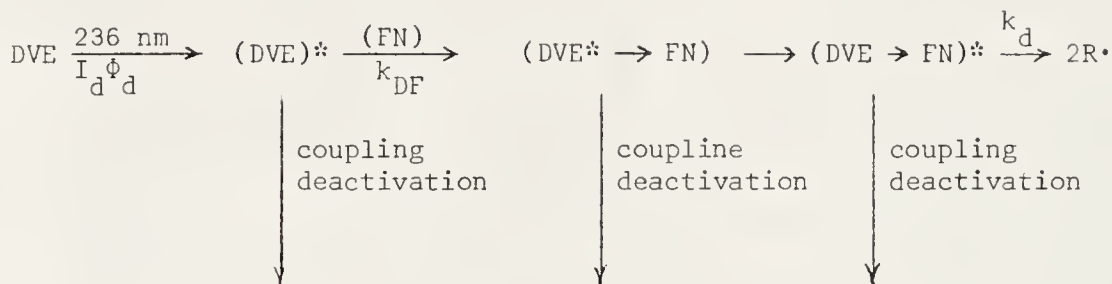
DVE* + FN

When f_d is kept constant,

$$\text{Rate } \alpha \; (DVE)^2(FN)/k_{rl}'(T) \; \alpha \; f_d^2(1-f_d)(T)^3$$

This is not consistent with the experimental results. The exciplex (DVE* → FN) can transfer into a lower energy state which is the excited complex (DVE → FN)*. All the excited states DVE*, (DVE*→ FN) and (DVE → FN)* are possibly deactivated by coupling with polar species

(monomers and complex)(Scheme IV).

$$DVE \xrightarrow[I_d \Phi_d]{236 \text{ nm}} (DVE)^* \xrightarrow[k_{DF}]{(FN)} (DVE^* \rightarrow FN) \longrightarrow (DVE \rightarrow FN)^* \xrightarrow{k_d} 2R\cdot$$

| coupling deactivation | coupline deactivation | coupling deactivation |

Ground State Molecules

Scheme IV

Taking this into consideration, the deactivation of excited states can be assumed to be proportional to $k_{rl}''(T)^n(FN)^m$ by the fact that both monomers and complex may deactivate all the excited complexes and FN is preferred to some extent.

Then,

$$R_i = \frac{k_d I_{abs} \Phi_c \epsilon_c (DVE)}{k_{rl}''(T)^n (FN)^m} \qquad (Eq. 25)$$

$$Rate = \frac{(DVE)^2 (FN)^{1-m}}{k_{rl}''(T)^n}$$

The rate maximum will be at

$$(FN)/(DVE) = \frac{1-m}{2} \quad , \text{ i.e., } f_d = 2/(3-m)$$

The contribution of FN to deactivation is partly included in $(T)^n$ term, it is reasonable to assume that $0 < m < 1$, therefore, $2/3 < f_d < 1$.

Although the exact position of the maximum rate at 236 nm was not known, a maximum at $f_d = 0.66-0.80$ was observed which was predicted by the proposed deactivation mechanism. When f_d is kept constant:

$$Rate \propto [f_d^2 (1-f_d)^{1-m} (T)^{3-m}]/[k_{rl}''(T)^n] \propto (T)^{3-m-n} = (T)^x \quad \text{where } x=3-m-n.$$

There are three excited states involved. It can be assumed that $3 > n > 2$.

Rate α $(T)^x$, where $x = 3 - m - n < 1 - m < 1$

This is the case observed for copolymerization at 236 nm where

Rate α $(T)^{0.77}$ (Table XVII and Fig. 17).

In Table XIV the rate ratio at $I = 8.86 \times 10^{14}$ photons/sec at 236 nm to the rate at 300 nm was the same as the quantum yield ratio. Apparently, the difference of the rate and quantum yield between 236 nm and 300 nm was based on the same factor, probably the initiation rate, because only the primary radical formation was a function of wavelength. By definition, quantum yield (Φ) is the number of copolymer molecules formed per photon absorbed.

Φ = No. of copolymer molecules formed/no. of photons absorbed.

   = No. of primary radicals formed per sec/no. of photons absorbed per sec.

   = R_i / I_{abs}

Therefore, from Eq. 24 and 25, when (DVE) = 0.71, (FN) = 0.47, (T) = 1.18.

$$\frac{\Phi_{300}}{\Phi_{236}} = \frac{R_{i300}}{R_{i236}} = \frac{\Phi_c k''_{rl} (T)^n (FN)^m}{\Phi_d \varepsilon_d (DVE) k_{rl}(T)} = \frac{\Phi_c k''_{rl}}{\Phi_d \varepsilon_d k_{rl}} (DVE)^{-1} (FN)^m (T)^{n-1}$$

By assuming that $3 > n > 2$, $m \simeq 1$, the two deactivation constants are similar in the order of magnitudes, $k''_{rl}/k'_{rl} \simeq 1$, and ε_d is in the order of $10^2 - 10^3$. Therefore, $(DVE)^{-1}(FN)^m(T)^n \simeq 0.78 - 0.92 < 1$

Then

$$\frac{\Phi_{300}}{\Phi_{236}} < \Phi_c/(\Phi_d \varepsilon_d) < (1/10^2 \times \Phi_c/\Phi_d) < 1$$

where Φ_c/Φ_d is less than 10^2.

Although the exact value of the parameters were not obtained, it is reasonable to say that Φ_{236} is larger than Φ_{300} and the same result applies for the rates where $\text{rate}_{300} < \text{rate}_{236}$ when compared at the same light intensity absorbed.

In conclusion, the proposed propagation process is consistent with the experimental results provided that the excited states are deactivated by collision with the monomers or complex and the proposed initiation process for photocopolymerization initiated by the charge-transfer complex mechanism. These postulations are also supported by the fact that the rate maximum at 236 nm for lower total concentration (0.6 m/l) was at the position between $f_d = 0.55$-0.80 and is less than that for higher total concentration ($f_d = 0.67$-0.80) for (T) = 2.00 m/l). At 236 nm,

$$R_i = \frac{k_d I_{abs} \Phi_d \varepsilon_d (\text{DVE})}{k''_{rl}(T)^n(\text{FN})^m}$$

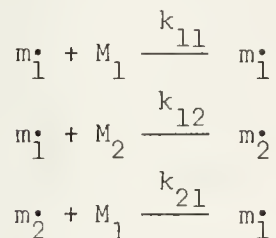due to the preference of FN in the deactivation processes, for lower concentration, this preference is lost and

$$R_i = \frac{k_d I_{abs} \Phi_d \varepsilon_d (\text{DVE})}{\cdot \; k''_{rl}(T)^n}$$

which leads to the maximum rate near $f_d = 0.67$. At 300 nm, the rate maximum is not dependent on the total concentration, indicating that there is no preference deactivation by FN. This can be understood on the basis that the electron distribution or energy distribution is more symmetric in excited complex (DVE $\rightarrow$ FN)* than in the exciplex (DVE* $\rightarrow$ FN). In the exciplex, partial excitation is localized on DVE part and deactivation is preferred by the opposite polar molecule such

as FN. Even more, the excited state of DVE is more preferable to de-activated by FN.

With the proposed mechanism, it is possible to calculate the reactivity ratio of k_{11}/k_{12}, i.e. the ratio of the reactivities of the complex and the acceptor toward the cyclized radical XXXI.

Considering the following reaction scheme:

$$m_1^{\bullet} + M_1 \xrightarrow{k_{11}} m_1^{\bullet}$$

$$m_1^{\bullet} + M_2 \xrightarrow{k_{12}} m_2^{\bullet}$$

$$m_2^{\bullet} + M_1 \xrightarrow{k_{21}} m_1^{\bullet}$$

where M_1 is the complex, M_2 is the acceptor, $m_1^{\bullet}$ is the cyclized radical, and $m_2^{\bullet}$ is the acceptor radical, and by assuming a steady state, a copolymer composition equation can be obtained with m_d as the mole fraction of DVE in the copolymer, (M_1) and (M_2) as the concentrations of M_1 and M_2, respectively.

$$\frac{m_1}{m_2} = \frac{-d(M_1)/dt}{-d(M_2)/dt} = \frac{k_{11}(M_1) + k_{12}(M_2)}{k_{12}(M_2)} = 1 + r_1 \frac{(M_1)}{(M_2)}$$

where r_1 is the reactivity ratio (k_{11}/k_{12}). After rearranging the above equation,

$$\frac{3m_d - 1}{1 - 2m_d} = r_1 K_c f_d(T)$$

By plotting the left hand side against f_d, the reactivity can be ob-tained from the slope, the equilibrium constant, K_c and the total concentration (T). In Table XVIII the calculated reactivity ratios are shown.

As shown in Fig. 18, the correlation coefficients are small. However, the estimated value for $r_1 K_c(T)$ can be obtained as in Table XVIII.

Table XVIII

The Determination of Reactivity Ratio r_1

f_d	At 300 nm		m_d	At 236 nm	f_d	With AIBN[a]	
	m_d	$\dfrac{3m_d-1}{1-2m_d}$		$\dfrac{3m_d-1}{1-2m_d}$		m_d	$\dfrac{3m_d-1}{1-2m_d}$
0.2	0.35	0.178	0.436		0.08	0.374	0.48
					0.2	0.383	0.64
0.4	0.412	1.34	0.400	1.00	0.4	0.383	0.64
				2.41	0.5	0.393	0.64
0.6	0.372	0.453	0.436	1.22	0.75	0.396	0.90
					0.85	0.41	1.28
0.8	0.410	1.28	0.408		0.95	0.45	3.50
$r_1 K_c(T)$	1.50		2.75				2.24
r_1	8[b]		13[b]				16[c]

[a] Ref. 32, the reaction was carried out in DMR with (T) = 1.1-4.5 m/l.

[b] (T) = 2.0 m/l, K_c = 0.10.

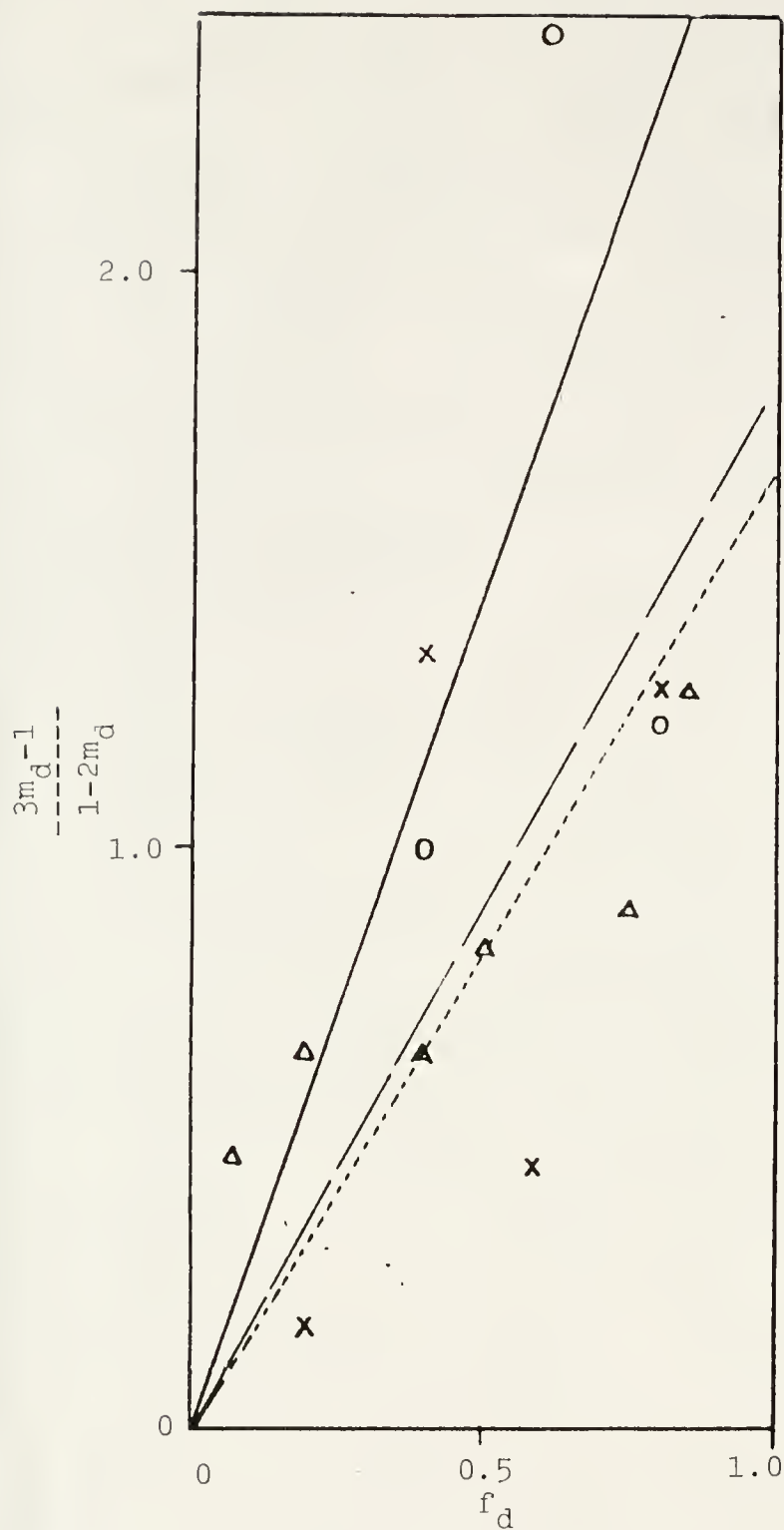[c] An average value of (T) is assumed as 2.8 m/l, the K_c is assumed as 0.05.

Fig. 18 The determination of reactivity ratios
———— (T) = 2.0 m/l, at 300 nm
- - - - - (T) = 2.0 m/l, at 236 nm
—·—— —— (T) = 1.1-4.5 m/l, with AIBN

A value approximately in the order of 10 was obtained, which is consistent with the assumption that the reactivity of the complex towards the cyclized radical is high and the relation $k_{11} >> k_{12}$ holds.

In summary of this chapter, a reaction mechanism including the participation of complex in both initiation and propagation was proposed and all the experimental results have been explained.

CHAPTER IV
EXPERIMENTAL

Materials

Fumaronitrile (from Aldrich), m.p. 94-5°C, and maleic anhydride (from Fisher), m.p. 56-7°C, were recrystallized from benzene and either sublimed before use or stored in a refrigerator. Divinyl ether (DVE) was prepared by dehydrohalogenation of bis(2-chloroethyl)ether (from Eastman) with KOH in triethanol amine at 170-90°C and redistilled before use.[81] Reagent chemicals were used for actinometry. Reagent grade azobisisobutyronitrile (from J.T. Baker) was recrystallized from reagent grade methanol, filtered and dried in vacuo in the presence of P_2O_5. The purified AIBN was kept in the refrigerator. For some syntheses and kinetic runs reagent grade solvents were purified by the following methods and distilled before use or stored in a desiccator in order to keep the solvent as dry as possible.

Benzene: Analytical grade benzene (from Mallinckrodt) was stirred with concentrated sulfuric acid for two days. It was then washed with dilute, aqueous KOH (5%) solution three times, followed by washing with water three times. The washed benzene was dried over Linde 3A Molecular Sieve and distilled over phosphorus pentaoxide in a nitrogen atmosphere, and stored in a colored bottle in the desiccator.

Acetone: Analytical grade acetone (from Mallinckrodt) was dried over Linde 3A Molecular Sieves and distilled from phosphorus pentaoxide or calcium hydride.

Acetonitrile: Analytical grade acetonitrile (from Mallinckrodt) was distilled from phosphorus pentaoxide. It was then refluxed over calcium hydride (5 g/liter) for at least an hour, then distilled slowly, discarding the first 4 and the last 10% of the distillate.

Xylene: Analytical grade xylene (from Mallinckrodt) was distilled over calcium hydride and only the middle cut was collected.

Chloroform: Analytical grade chloroform (from Mallinckrodt) was shaken with concentrated sulfuric acid, washed with water, dried over calcium chloride and distilled over calcium hydride.

Diethyl ether (from Mallincdrodt) was distilled over calcium hydride.

Tetrahydrofuran: Analytical grade tetrahydrofuran (from Mallinckrodt) was refluxed and distilled over lithium aluminum hydride just before use.

Equipment and Data

For photolytic reactions, the glassware was cleaned with acidic di-chromate solution, then washed and dried in an oven overnight.

Melting point determinations below 250°C were carried out in open capillary tubes in a Thomas-Hoover Melting Point Apparatus. The melt-ing point determinations over 250°C were carried out on a Fisher-Jones Melting Point Apparatus.

All temperatures reported were in degrees centigrade and were uncorrected. Pressures were expressed in millimeters of mercury, having been determined by means of either a Zimmerli or McLead Gauge.

Infrared spectra were obtained with a Beckman IR-8 or IR-10 Double-beam Infrared Spectrophotometer. Ultraviolet spectra were run on a Beckman-DK-2A Double-beam Recording Spectrophotometer.

60 MHz Nuclear Magnetic Resonance (nmr) spectra were obtained on a Varian Associates Analytical NMR Spectrometer, Model A-60. ^{13}C Nmr

spectra were recorded on a Varian XL-100 pulse-FT spectrometer at 25.16 MHz, using broad-band decoupling at 100 MHz.

Intrinsic viscosities were calculated from efflux times of solutions through a Cannon-Ubbelohde Semi-micro Dilution Viscometer placed in a 30°C to 1°C constant temperature water bath.

Copolymer composition was calculated from carbon and/or nitrogen analysis by Heterocyclic Chemical Corp., Galbraith Laboratory, Inc., or PCR Microanalytical Laboratories. The copolymers of DVE-MAH and DVE-FN were found almost invariably to be associated with water. The copolymer samples sent for analysis were purified at least twice by precipitation followed by drying in vacuo at 56°C or 50°C for more than 3 days.

Irradiation Source

For synthetic experiments above 300 nm, a Hanovia High Pressure Mercury lamp (450 Watts, cat. no. 679 A-36) equipped with quartz water cooling system was employed as the light source.

For monochromatic light irradiation, the source was a 2500 Watt Mercury Xenon lamp (Hanovia type 929B-9U) contained in the Schoeffel LN 152N/2 Lamp Housing (supplied with 2 1/4" diameter variable focus double quartz condenser, parabolic reflector, cooling fan, and finned heat sinks for the arc lamp). The output beam is deflected through a Schoeffel LHA 165/2 Stray Light Reducing and Illumination Predispersion Prism, assembly into a Schoeffel GM 250 High Intensity Monochromator (focal length 0.25 m, linear dispersion 3.2 nm/mm, grating blazed at 300 nm with 1180 grooves/mm, aperture ratio f/3.9). The power supply for the lamp is a Schoeffel CPS 400 equipped with the Schoeffel LPS 400S starter with operates the lamp at 50 V and 50 A.

UV Studies

The spectrometric studies of complexations were carried out with a Beckman DK-2A Spectrophotometer with quartz cells with 1 cm pathlength. For studying pure DVE and FN, pure acetonitrile was used as reference. For the studies of the complex, the reference cell was filled with FN in acetonitrile at the same concentration as in the complex solution cell. The absorbance of pure DVE at the same concentration was deducted from the absorbance measured because FN and DVE present some residual absorption below 300 nm. The exact value of the absorbance of the complex could be evaluated. The conditions of measurements are shown in the respective tables and figures in the text.

Syntheses Related to Monomer Preparation

Divinyl Ether

This compound was prepared following the procedure of Shastakuvskii and Dubrova.[81] A 3 liter, three-necked flask was equipped with a mechanical stirrer, an addition funnel, a reflux condenser and a thermometer. Into this flask was placed 1000 g (17.8 mole) of analytical grade potassium hydroxide and 200 g (1.41 mole) of triethanol amine. With the object of removing divinyl ether from the sphere of reaction as fast as it was formed, warm water (35°C) was passed through the reflux condenser, which was connected to a condenser with ice water cooling. A two necked round bottom flask as receiver was connected to this distillation condenser and immersed in an ice water bath. The second neck of the receiver was connected with a drying tube. The mixture of potassium hydroxide and triethanol amine was preheated until KOH was melted (about 190-210°C). With stirring, 400 g (2.79 mole) of bis(2-chloroethyl ether, b.p. 91°C/37mm) was added slowly from the

addition dropping funnel to the alkaline solution with the mixture
temperature between 160 and 190°C. A white fume, which was tested as
basic, was observed right after the addition. Liquid DVE was collected
two hours after all starting material was added. Further refluxing did
not improve the yield significantly. The product was washed three
times with precooled water to prevent evaporation of DVE. Then, after
washing three times with cold hydrochloric acid (5%), followed by
washing three times with cold deionized water, the resulting organic
layer was dried over calcium chloride overnight. After refluxing and
distilling over calcium hydride, the product was kept in the refrigera-
tor. The purified product was 75 g (27% yield) of pure divinyl ether,
b.p. 29-29.5°C. The literature gave b.p. 28-29°C. The ir spectrum was
identical to the reported spectrum. Nuclear magnetic resonance spectrum
(Fig. 19a) showed a clear ABX pattern in the olefinic hydrogen region.
Little or no impurities were detectable in the nmr spectrum.

Bis(2,2-didetueriovinyl)ether

  2,2,2',2'-Tetradeuteriodiethylene glycol.[50] A 300 ml three necked
round bottom flask was equipped with a reflux condenser, an addition
funnel, a mechanical stirrer, and an inlet for maintaining a slightly
positive dry oxygen-free nitrogen pressure. To 200 ml of THF which was
freshly distilled from lithium aluminum hydride, was added 8 g of
lithium aluminum deuteride (0.19 mole). The mixture was stirred under
reflux for 30 minutes. Sublimed diglycolic anhydride (18.4 g, 0.16 mole)
(from Aldrich), m.p. 92-93°C, dissolved in 150 ml of freshly distilled
THF, was added with stirring at a rate maintaining gentle reflux. The
mixture was stirred with refluxing under nitrogen overnight. After
cooling, the reaction mixture was hydrolyzed with 30 ml of deionized
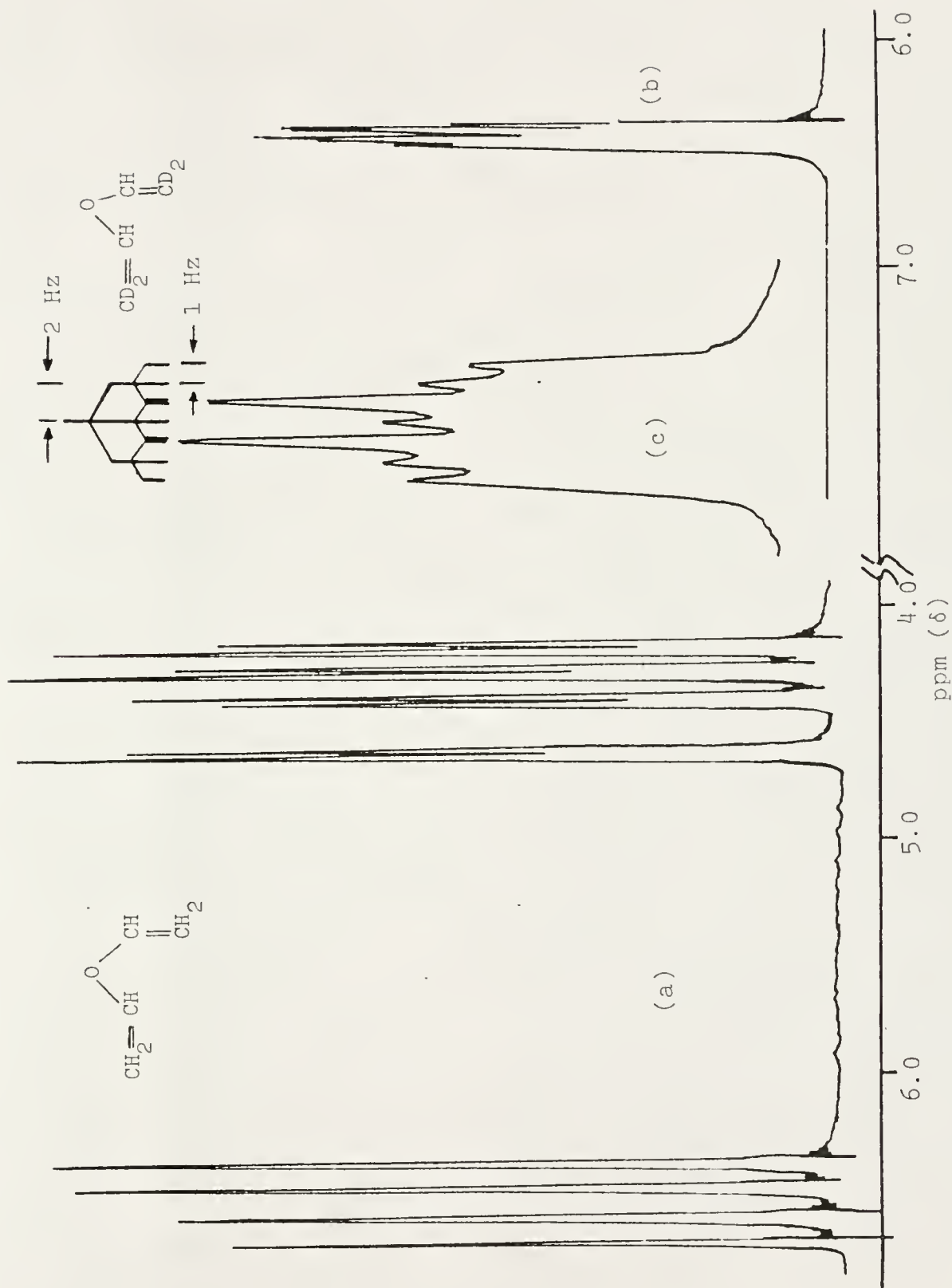
Fig. 19 60 MHz nuclear magnetic resonance spectra of (a) DVE, (b) DDVE with 250 ppm sweep width, (c) DDVE with 100 ppm sweep width.

water in ice bath. After the ice bath was removed, the mixture was stirred for 10-20 minutes. The precipitate was filtered out and stirred with 30 ml of 0.6 N sulfuric acid and 100 ml of THF. The mixture was filtered. After extracting the solid three times with 100 ml of THF, the resulting extracts were combined with the previous filtrates and dried with excess anhydrous potassium carbonate overnight with stirring. THF was rotavapped and a slightly yellow oily compound with some solid suspension was left. This compound was carefully filtered and distilled under vacuum. A colorless compound was collected at b.p. 102-105°C/1mm, yield 8.6 g (49%). The ir spectrum of this product was similar to diethylene glycol but with new absorption bands at 2220 and 2110 cm^{-1}.

The ir spectrum (neat) of the compound showed absorption bands at 2840-2980 (s,b), 3040-3520 (s,b), 2220 (m), 2110 (m), 1740 (m, multiple), 1650 (m, multiple), 1350 (m with shoulder around 1450), 1260 (m), 1170 (s), 1110 (s,b), 1030 (m), 970 (m), 850 (m,b), 800-600 (s, broad with shoulder at 800 cm^{-1}).

The nmr spectrum (Fig. 20a) ($CDCl_3$) of the compound showed a singlet peak at δ 4.45 and 3.58 ppm, with an area ratio 1:2. In contrast, a multiple absorption centered at δ 3.65 ppm was observed in diethylene glycol with a ratio of 4:1 to the singlet at δ 4.94 ppm.

The same procedure was applied to prepare diethylene glycol from diglycolic anhydride and lithium aluminum hydride. The resulting product (b.p. 97-101°C/1 mm, reported 110°C/3 mm) showed exactly the same ir and nmr spectra as the literature.

Bis(2-bromo-2,2-dideuterioethyl)ether.[51]   Phophorus tribromide (23.8 g, 0.09 mole) was placed in a flask equipped with a mechanical stirrer, dropping funnel, and a reflux condenser with a calcium chloride tube.
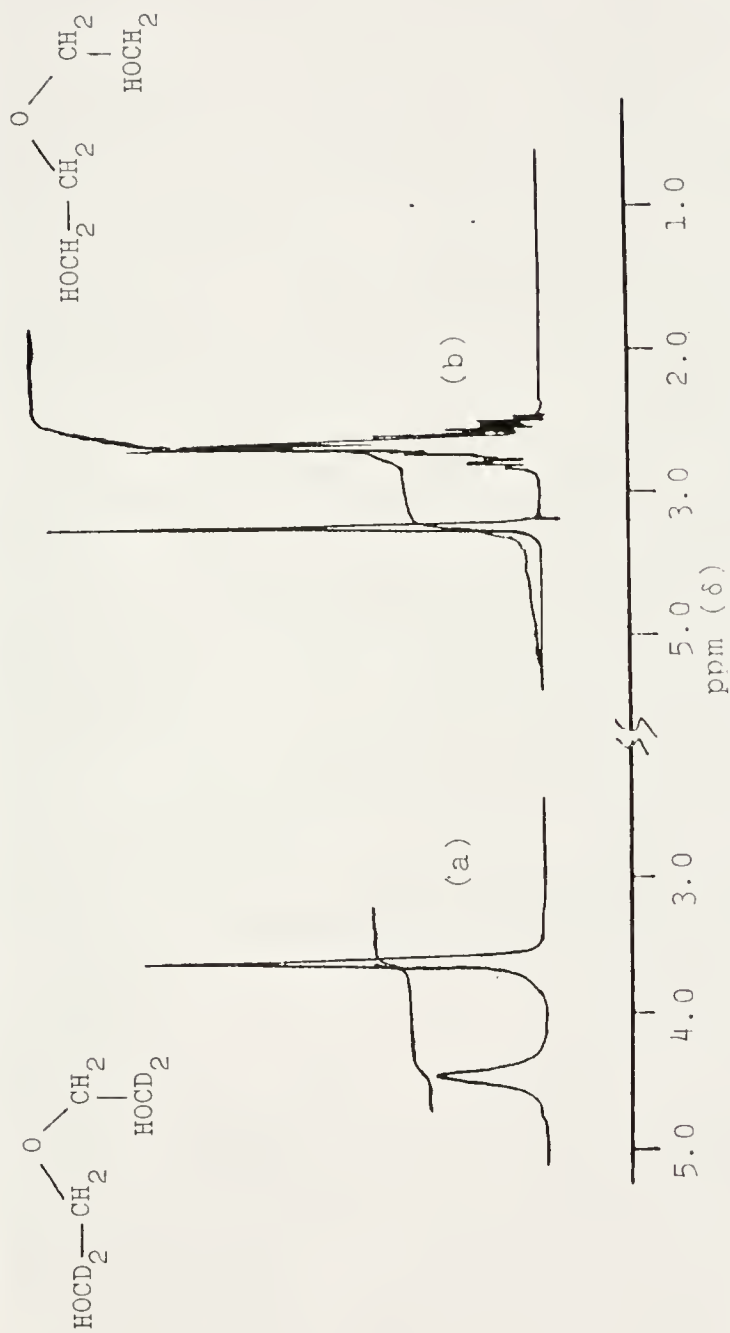
107

Fig. 20 60 MHz nuclear magnetic resonance spectra of (a)
2,2,2',2'-tetradeuterodiethylene glycol, (b) diethylene
glycol.

A solution of 11.7 g (0.11 mole) of bis(2,2-dideuterioethyl)ether in 3.3 g (0.04 mole) of freshly distilled pyridine was slowly added with dry ice-acetone cooling. The mixture was left overnight and warmed up to room temperature. The liquid portion was extracted with ether, washed with 0.1 N hydrochloric acid and water and dried with anhydrous sodium sulfate. After filtration, the filtrate was distilled under vacuum after rotavapping the ether. The product was collected at 75-77°C/3.5 mm. Yield: 19.1 g, 76%.

The ir spectrum of the product was similar to the nondeuterated bis(2-bromoethyl)ether, but with a new absorption band at 2170 cm^{-1}.

The ir spectrum (neat) of the compound showed the absorption bands at 2850-2950 cm^{-1} (m,b), 2171 cm^{-1} (weak), 1470 (m, multiple), 1360 (m), 1285 (m), 1260 (m), 1140 (m), 1105 (s, multiple), 1000 (m), 930 (m), 180 (w) cm^{-1}.

The nmr spectrum (neat) of the compound showed only a clear sharp singlet at δ 3.80 ppm with half width 3 ppm (Fig 21a).

This same procedure was applied to prepare bis(2-bromoethyl)ether from diethylene glycol. The resulting products (b.p. 92-3°C/12mm, lit. 115°C/32 mm)[82] showed exactly the same ir and nmr spectra as in the literature with a clear AA'BB'.nmr absorption pattern. (Fig. 21b).

Bis(2,2-dideuteriovinyl)ether. Similar to the preparation of divinyl ether from dichloro starting material,[81] 21.7 g (0.39 mole) of potassium hydroxide and 11.8 g (0.083 mole) of triethanol amine was added into a 50 ml three necked round bottom flask equipped with a mechanical stirrer, an addition dropping funnel, thermometer and a 35°C reflux condenser which was then connected to a distillation condenser leading to two necked receiver with drying tube. Purified bis(2-bromo-2,2-dideuterio-
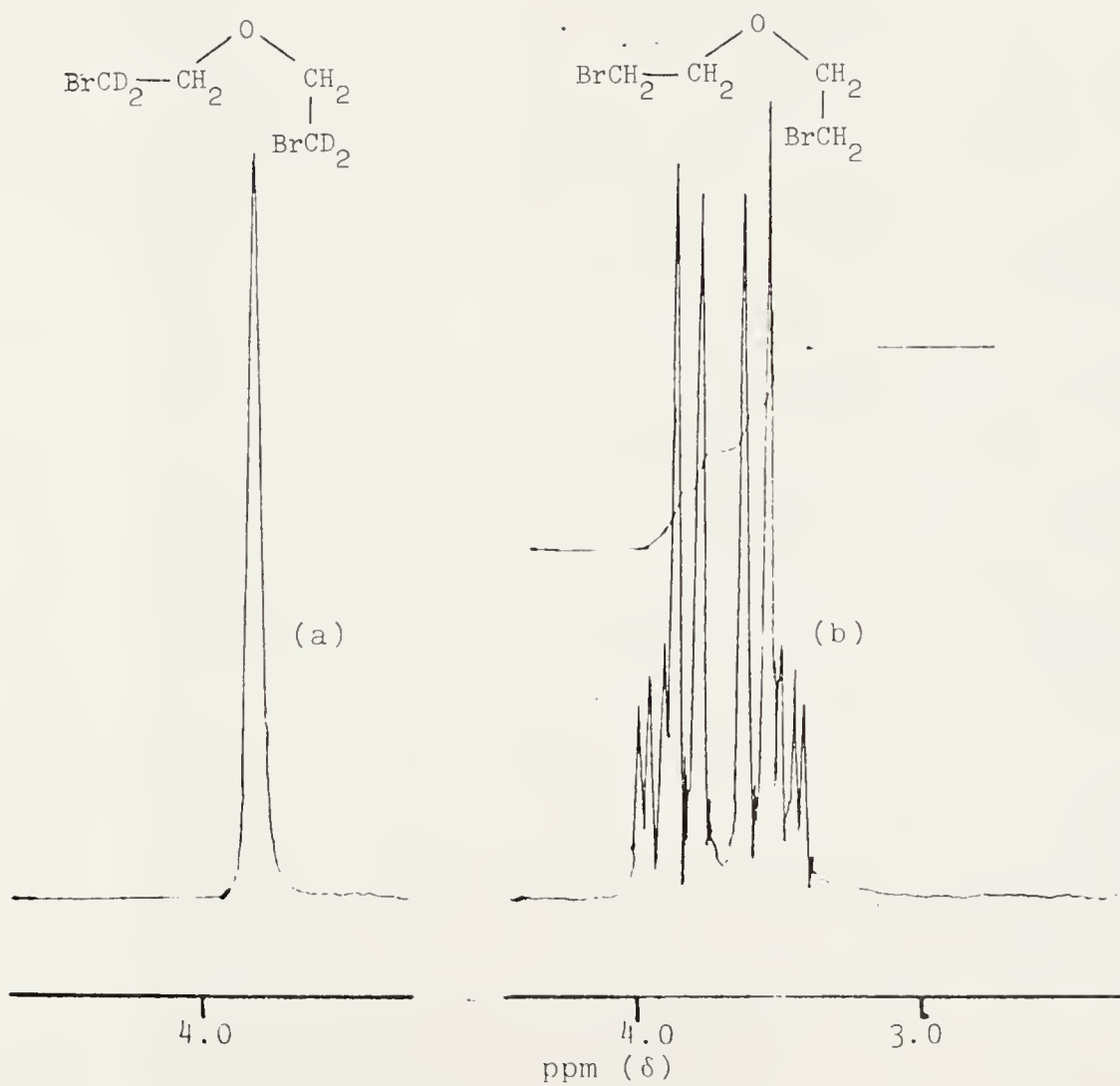
Fig. 21   60 MHz nuclear magnetic resonance spectra of (a)
bis(2-bromo-2,2-dideuteroethyl)ether, (b) bis(2-bromoethyl)
ether.

ethyl)ether (18.3 g, 0.078 mole) was added to the melting mixture at 190°C. The product was washed with deionized water and distilled over calcium hydride. Yield: 1.5 g (26%) purified product, B.p. 30-31°C.

The nmr spectrum (neat) (Fig 19b) of the compound showed a multiplet centered at δ 6.4 ppm instead of the ABX pattern of divinyl ether. Only a little impurieties were observed on the nmr spectrum. The multiplet was further examined with 100 cps sweep width; a clear splitting pattern was observed with a ratio of approximately 1:1:2:1:2:1:1 corresponding to a H-D $\underline{cis}$ coupling and H-D $\underline{trans}$ coupling with $J_{HDcis}=1$ Hz and $J_{HD, trans} = 2Hz$, respectively.

This same procedure was applied to prepare divinyl ether from bis(2-bromoether)ether. Divinyl ether was obtained as confirmed by the ABX pattern on nmr spectrum.

Copolymerization

Photocopolymerization of DVE-FN System

General photocopolymerization procedure. DVE and FN were weighed and dissolved in the solvent in volumetric flasks. The solutions were transferred to Pyrex or Quartz tubes. The contents of the tubes were frozen with liquid nitrogen and the tubes were evacuated on a vacuum line. The freeze-pump-thaw cycle was repeated at least three times under pressure of 10^{-5} mm Hg or better and the tubes were then sealed. The quartz tubes (21 mm o.d.) were joined to a Pyrex section by graded seal. The tubes were irradiated for a period of time, while being rotated on their axis by a rotavapor motor (Buchi Corp.) or an electric motor. A lens supplied by Schoeffel Co. transforms the exit beam of the monochromator into a thin line such that only the center portion of the tube is irradiated. The polymerization rate of the polymer was

measured by precipitation and weighing after evaporation of the
irradiated solution and drying in a vacuum oven for at least 4 hours
at 50°C. The results were shown earlier.

Copolymerization with additives. Some additives has been added into
DVE-FN system. The results are listed in Table XIX.

Table XIX

The Copolymerization of DVE-FN System with Additives

Additives	Concentration m/l	Wavelength nm	Yield/min. mg/min
No additive		236	0.036
		300	0.36
NEt$_3$	0.1	236	0
		300	0
	0.01	236	0
		300	nil
DPPH	0.009	236	0
		300	0
	3.5×10^{-5}	236	0.035
		300	0.129
Chloranil	0.006	363	0

Note: 1. [DVE]=[FN]= 0.6 m/l.
       2. DPPH is diphenyl picryl hydrazyl radical.

The light intensity and the quantum yield measurement. The intensity
of the light absorbed by the comonomer solution during photocopolymeriza-
tion was measured in the same reaction tube. After the irradiation of
sample, the tube was emptied and filled in the dark with known amounts

of the actinometer solution by pipettes. In the tube which holds 15 ml

solution, the following procedure was used.

To the tube which may be wet after having been washed with water

in the dark was pipetted 15.0 ml of the actinometer solution and

irradiated for an exact period of time according to the wavelengths.

After irradiation, the contents were poured into a 50 ml volumetric

flask through a funnel to avoid spillage and rinsed twice with about

5 ml portions of distilled water. To the irradiated actinometer

solution and a dark standard was added 2 ml of the 0.1% phenanthroline

aqueous solution and 10 ml of the NaOAc-H_2SO_4 buffer solution, and

diluted to the mark with distilled water. The solutions were left at

least one hour or overnight in the dark. The Beckman DK-2A ultraviolet

spectrophotometer was zeroed at 510 nm using the dark standard sample

in the sample and reference beams. Each irradiated actinometer solution

was analyzed at 510 nm on the absorption scale.

To calculate the light intensity:

photons/min = 6.02×10^{20} VA/lε x 1/Ψt

A = Volume of the actinometer solution whose absorption was
measured = 50.0 ml.

l = Path length of the cell = 1.0 cm.

ε = Extinction coefficient of the actinometer = 11100.

Ψ = 1.24 and 1.25 at wavelengths larger and smaller than 254 nm,
respectively.

t = Time the actinometer was irradiated.

The irradiation time was adjusted so that the absorbance was around

0.6-0.8. The quantum yield of the photocopolymerization could be

obtained.

Φ = No. of copolymer molecules produced/no. of photons absorbed.

= Wt. of copolymer/average molecular weight of the copolymer

6.02 x 10^{23}/It$_{ir}$

I = Light intensity absorbed by the actinometer solution.

t$_{ir}$ = The time polymerization solution was irradiated.

For DVE-FN system, the average molecular weight of the copolymer was obtained by Zeegers and Butler as 4600 and 5500 at the total concentration of 1.2 m/l and 1.8 m/l, respectively.[39] For other concentrations the molecular weight may be slightly different, but within the same order.

The preparation of actinometer solution.[82] The solution was prepared by dissolving 295 mg of the $K_3Fe(C_2O_4)$ crystals, in 80 ml of distilled water, followed by adding 5 ml of 1 M H_2SO_4 and diluting to 100 ml mark. All operations were made in the dark with an infrared light. The buffer solution was prepared by dissolving 81.7 g of NaOAc in 600 ml of water. The solution was filtered into a 1000 ml volumetric flask, 180 ml of 1 M H_2SO_4 was added, and diluted to the mark.

The Synthesis of Copolymer of DVE-FN System

For synthetic runs for this system, the reactions were allowed to proceed more than 40% in order to get large enough amounts of sample for ^{13}C nmr spectroscopy and other analyses. In general, a 0.6 m/l of DVE and 0.6 m/l of FN solution was prepared in acetonitrile with or without 3.1 x 10^{-3} m/l of AIBN. After three freeze-pump-thaw cycles, the sample was sealed. For 236 nm, the Schoeffel set up was used to irradiate the sample in quartz tube for 24 hours; 40% conversion was obtained. For 300 nm, the Hanovia high pressure mercury lamp (450 Watts) was used to irradiate a sample in a pyrex tube at room temperature, so that light

with wavelength shorter than 310 nm was filtered out. After 17 hours irradiation, 55% conversion was obtained. For free radical initiation, the sample was heated in an oil bath at 63°C for 10 hours; 44% yield was obtained. The resulting polymers were purified at least twice by dissolving in acetonitrile and precipitating from methanol. They were dried at 56°C in vacuo overnight. The analyses were shown earlier in the text.

Copolymerization of DVE-MAH System

General copolymerization procedure. A three necked round bottom flask was equipped with a mechanical stirrer, a nitrogen inlet and a rubber septum. The nitrogen inlet was connected to a trap filled with molecular sieves (4A) leading to a water free nitrogen source with a concentrated sulfuric acid bubbler. The flask was flushed with nitrogen for one hour with the septum open. With positive nitrogen flow, an appropriate amount of MAH (usually 1.96 g) was added followed by 35 ml of dry solvent, and the septum was replaced. In a 25 ml two necked pear shaped flask, an appropriate amount of AIBN (usually 13.6 mg) was added under positive nitrogen flow. Both necks were then sealed with septums. Usually, 1 ml of purified DVE was added through the septum with a syringe, followed by 5 ml of the dry solvent. The 100 ml reaction flask was preheated to the desired temperature by means of a constant temperature oil bath. With stirring, the DVE-AIBN solution was added through the septum by syringe as quickly as possible. After stirring for an appropriate time, the reaction was stopped by cooling with an ice bath and the septum was opened. The contents were filtered with a sintered glass filter (5 ml, medium porocity) and washed with dry diethyl ether. The resulting solid was purified at least once by dissolving in

dry acetone and precipitating from diethyl ether. It was then dried
at 50 or 56°C in vacuo for 3 days.

In this preparation the concentrations of MAH, DVE, and AIBN were
approximately 0.50, 0.28, and $2.1-2.5 \times 10^{-3}$ m/l, respectively.

For photocopolymerization at wavelengths longer than 300 nm,
a sample was prepared in the same manner as described for DVE-FN
system. The results are listed in Table XX.

It was observed that part of the copolymer prepared in benzene was
not soluble, especially with higher conversion. The resulting soluble
copolymer dissolved only in very polar solvents such as DMSO and DMF.
The DMSO solution of the copolymer from the higher conversion experi-
ments behaved irregularly on viscosity measurements, (Fig. 22).
It was then necessary to prepare soluble copolymer in solvents with high
chain transfer character. The results are shown in Table XX.

The Copolymerization of MAH with Bis(2,2-dideuterioethenyl)ether in
Cyclohexanone

The same procedure as described for DVE-FN system was applied for
the radical initiated copolymerization of bis(2,2-dideuterioethenyl)ether
with MAH in cyclohexanone. Deuterated DVE (0.2782 g) was reacted with
0.9128 g of MAH in the present of AIBN (2.4×10^{-3} m/l) in cyclohexanone
at 72°C for 2 hours. Yield: 1.01 g (85%). The copolymer was purified
by dissolving in dry acetone and reprecipitating from dry diethyl ether.
It was then dried under 10^{-5} mm Hg at 50°C for 3 days.

Table XX

The Copolymerization of DVE-MAH System at Different Temperatures

Solvent	Temperature	Concentration(m/l) DVE	FN	Initiation[c]	Time min.	Yield %	Viscosity[a]	Solubility in DMSO	Composition C%	H%	Cl%
Benzene	51-54	0.25	0.50	AIBN	125	25	1.2	Partially	43.83	5.16	
Benzene	60-66				100	85		Insoluble			
Benzene	61-64				47	47	1.4	Partially	44.19	5.14	
Benzene	61-62				32	24		Soluble			
Benzene	71-73				82	86		Insoluble	44.42	4.96	
Benzene	76-78				25	77	1.2	Soluble			
Benzene	28-29			≥310 nm	600	10		Soluble			
					1140	31	0.16[b]	Soluble	50.49	4.23	
Xylene	128-132	0.28	0.50	AIBN	15	62		Soluble	53.75	3.99	
Xylene	100-104	1.12	0.50		15	51		Soluble			
$C_6H_{10}O$[d]	70-72	0.50	0.95		120	81		Soluble			
$CHCl_3$	60-61	0.28	0.50		35	43	0.22[b]	Soluble	49.91	4.52	0.97
Xylene	29-30	1.12	0.50	≥310 nm	990	44		Insoluble	52.10	4.27	
$CHCl_3$	25-26	0.32	0.50	AIBN+≥310nm	60	81		Soluble	50.85	3.90	
$CHCl_3$				≥310 nm	240	56		Soluble	52.27	3.84	

See next page for footnotes.

Table XX (continued)

[a] The reduced viscosity at the concentration between 0.275 g/100 ml and 0.40 g/100 ml in DMSO.

[b] Intrinsic viscosity in DMSO at 30°C.

[c] AIBN concentration is $2.1-2.5 \times 10^{-3}$ m/l.

≥310 nm: Initiated with 450 Watts Mercury Lamp in a pyrex tube.

AIBN + ≥310 nm: Initiated with light in the presence of AIBN.

[d] Cyclohexanone.
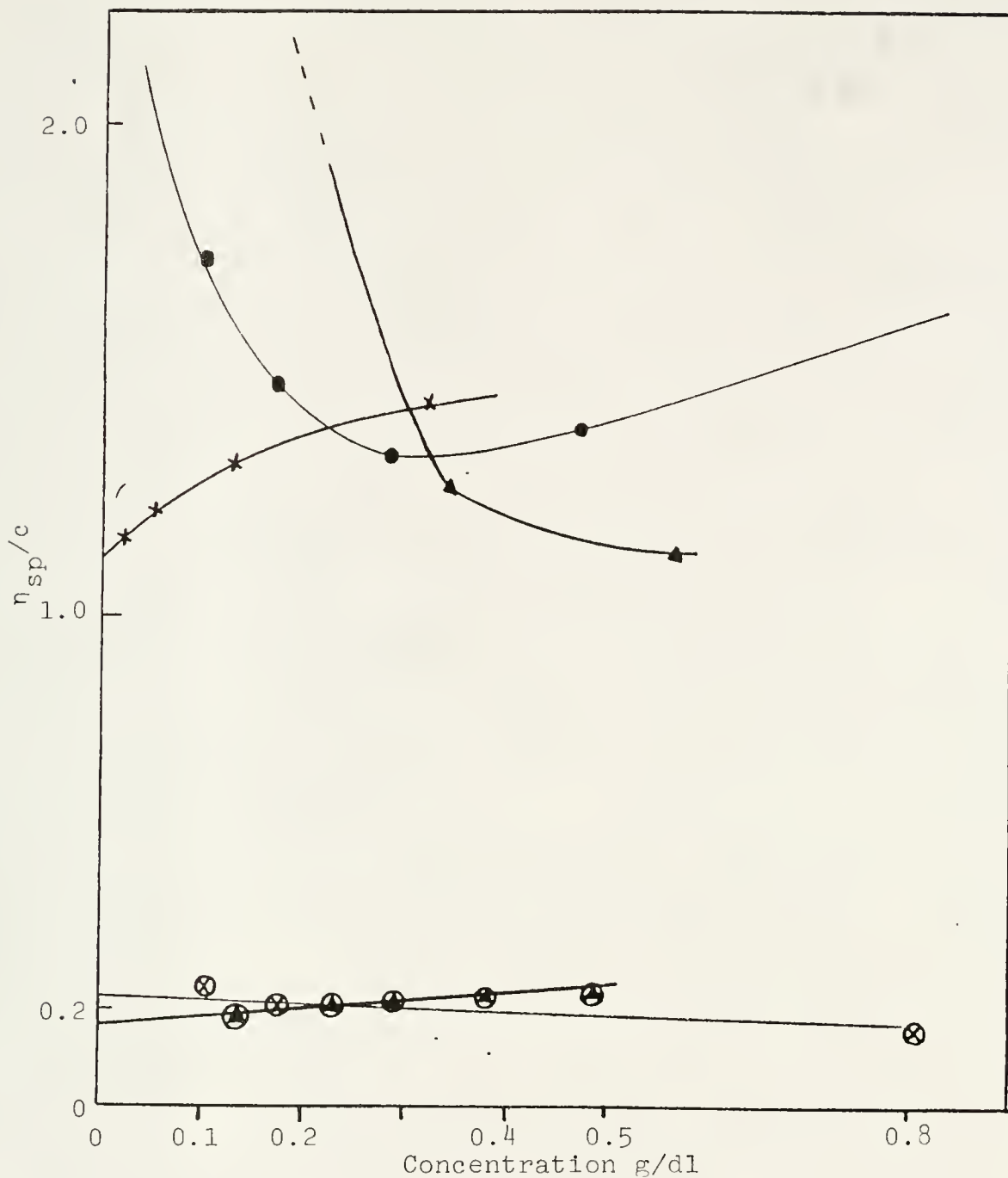
Fig. 22 The viscosities of the DVE-MAH copolymer in DMSO prepared in (a) benzene at 76-78°C with 77 % conversion, (b) benzene at 51-54°C with 25 % conversion, (c) benzene at 61-64°C with 47 % conversion, (d) $CHCl_3$ at 60-61°C with 43 % conversion, (e) benzene at 28-29°C with 31 % conversion initiated by light.

STEREOCHEMISTRY BACKGROUND FOR 5,5- AND 5,6-BICYCLIC SYSTEM
IN THE COPOLYMER OF DVE-MAH

Considering the stepwise cyclization involved in the cycloco-
polymerization described in equation 26, and that the two possible
bicyclic radicals may lead to a cyclocopolymer containing both bi-
cyclic structures:


(Eq. 26)
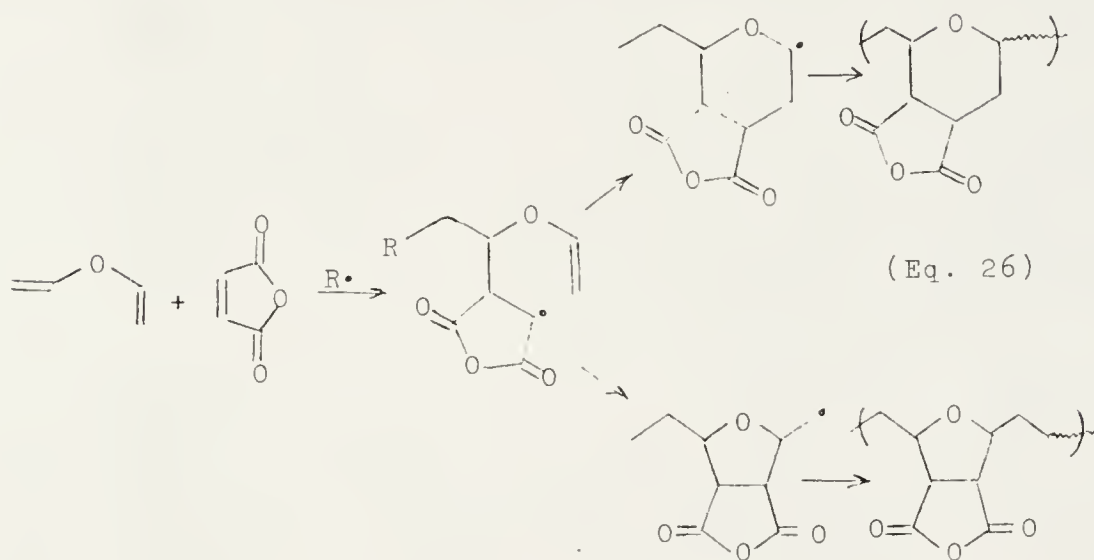
The following discussion is presented.

In each bicyclic structure, the rings can be fused by either <u>cis</u>
or <u>trans</u> junctions, and in each type of fused ring, system there are
several possible configurational isomers. All the possible configura-
tional isomers are listed below:

5,6-Bicyclic Ring System

Trans-fused ring system
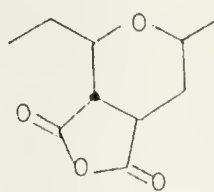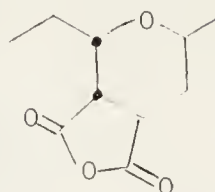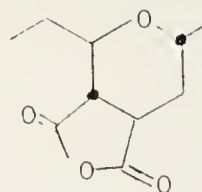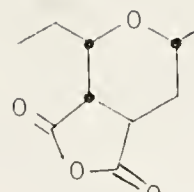
XI_a   XI_b   XI_c   XI_d
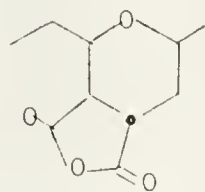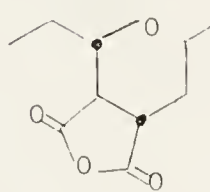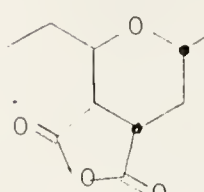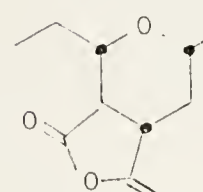
XI_e   XI_f   XI_g   XI_h

Cis-fused ring system
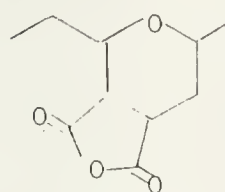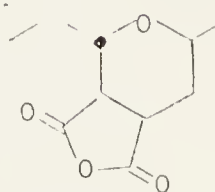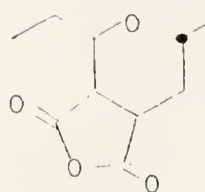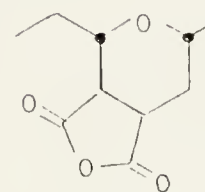
XII_a   XII_b   XII_c   XII_d
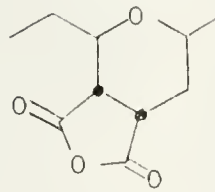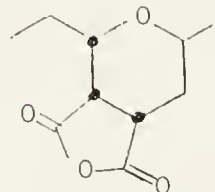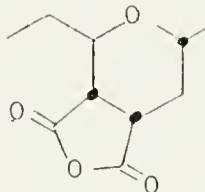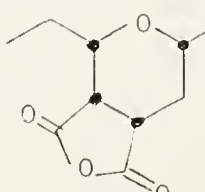
XII_e   XII_f   XII_g   XII_h

5,5-Bicyclic Ring System

Cis-fused ring system
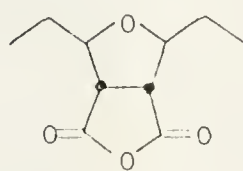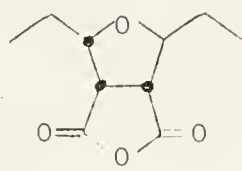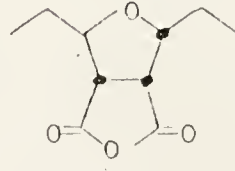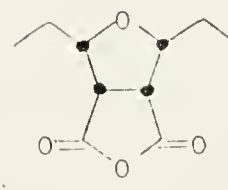
XIII_a   XIII_b   XIII_c   XIII_d

By use of models to compare the strain developed in these different configurations, it is reasonable to compare the models with the substituents on equatorial or pseudo equatorial positions based on the smallest steric 1,3-interaction expected.

In the 5,6-bicyclic ring system, there are eight possible configurational isomers for both cis and trans fused ring systems. The trans isomers are more rigid and more ring strain is expected in these systems. However, the energy differences between trans and cis isomers may be small. Although trans-bicyclio(4.3.0)-nonane is more stable (about 1 Kcal/mole) than the cis isomer, the cis hexahydrophthalic anhydride is more stable.[83] It is thus possible that both trans and cis isomers may be formed in the cyclocopolymerization.

Consideration of the very large substituents on the 2,6-position leads to Structures XIa and XIIe as the most plausible configurational isomers of cis and trans isomers, respectively. In these structures, the pyran oxygens are anti and syn to the anhydride ring system, respectively. In all cases the methine hydrogens on the 2,6-positions are non-equivalent and should experience different chemical shifts in the nmr spectra. All the other configurational isomers are possible to some extent. It is assumed that the presence of the other isomers only broaden the signals of the two methine hydrogens and for the same reason the two methylene groups are broadened.

The cis isomer for the 5,5-bicyclic system is much favored over the trans isomer. The heat of combustion of trans bicyclo(3.3.0) octane is greater than the cis isomer by 6 Kcal/mole.[60] There are four cis isomers possible. The cis isomers with cis-2,5-substitutions (XIVd) is most probable with oxygen anti to the anhydride unit. In this isomer,

the two methines as well as the two methylene groups are equivalent.
A very small difference is expected between anti and syn cis-di-2,5-
substituted cis-fused bicyclic systems because of the rapid inversion of
the C-O-C linkage relative to the anhydride unit. The isomers with
trans 2,5-disubstitutions are possible but some strain is developed in
order to position the two huge substituents on the pseudo equatorial
positions of the half-chair conformation.[64]

In conclusion, quite a few of 5,6-bicyclic isomers are expected
for both cis and trans fused ring systems and the overall consequence
is the non-equivalency between the 2- and 6-methine hydrogens, which
would lead to two broad signals in the nmr spectra. Only cis-fused
5,5-bicyclic ring system is expected and the most probable configura-
tional isomer could be expected to be a mixed anti and syn cis-2,5-
disubstituted cis-fused 5,5-bicyclic system. This system would lead
to a sharper peak in the nmr spectra. The presence of the possible half-
chair trans 2,5-disubstituted isomers would broaden the signals or even
show up as another signal. No trans-fused 5,5-bicyclic system seems
possible.

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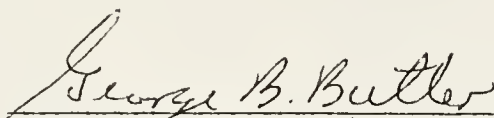
BIOGRAPHICAL SKETCH

Yuan Chieh Chu was born November 16, 1943, at Chian-Du, Chian-Su, China. In June of 1963, he graduated for the Normal University Secondary School in Taipei, Taiwan. He received the degree of Bachelor of Science with a major in chemistry from Chung Yuan Institute of Science and Engineering, Chun-Li in June, 1969. He attended the Graduate School of the National Taiwan University where he was awarded the degree of Master of Science in Organic Chemistry in June, 1971.

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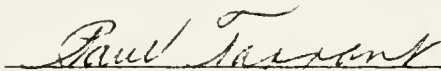
The author was married to the former Rolan Liu on October 24, 1973, in Gainesville, Florida. He is the father of one lovely child, Lawrence Chu.

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George B. Butler, Chairman
Professor of Chemistry

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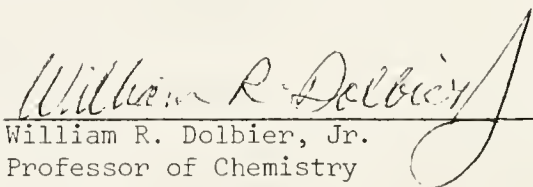
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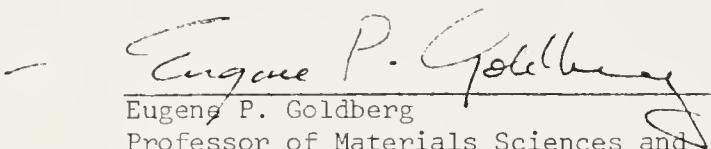
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